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PYROLYSIS OF THE LOWER PARAFFINS

V. THE CONVERSION OF THE GASEOUS PARAFFINS TO AROMATICS IN BAFFLED METAL TUBES AND THE CHEMICAL COMPOSITION OF THE PRODUCTS[1]

BY ADRIEN CAMBRON[2] AND COLIN H. BAYLEY[3]

Abstract

The thermal conversion of propane to aromatics has been investigated by passing the gas through externally heated alloy steel tubes under conditions of turbulent flow. Recycling experiments carried out under pressure have shown that, when the gas flow is turbulent, high rates of conversion can be obtained at temperatures as low as 800–810° C. Heat resistant chromium-nickel alloys of the 18 : 8 type have been found unsuitable for this purpose owing to the catalytic formation of carbon. Yields of 23.3 lb. of light oil per 1,000 cu. ft. of propane put through were obtained at 800° C. together with 10 lb. of liquids boiling above 200° C. The composition of the liquids obtained in these experiments has been determined by fractionation and chemical methods. The light oil obtained under the above conditions contains about 64% benzene, 14% toluene, 7.8% styrene and small amounts of cyclopentadiene, xylenes and higher aromatics. The liquids boiling above 200° C. contain about 25% naphthalene and 12.5% anthracene together with smaller amounts of mono- and dimethyl naphthalenes, acenaphthene and phenanthrene.

A considerable number of investigations have been reported in the literature on the conversion of the higher gaseous paraffins to aromatics. In most of these investigations silica or porcelain tubes were used, but a few experimenters, in particular Zanetti (23), determined the effect of carrying out the thermal treatment of hydrocarbon gases in metal tubes, or in the presence of metals, such as copper, iron or nickel. The work done on the subject up to 1929 is comprehensively reviewed in a survey published by Hague and Wheeler (13), who included in their paper the results of their own experiments in silica and porcelain tubes, and their conclusions as to the probable mechanism of the formation of aromatics from gaseous paraffins at high temperatures. Chamberlin and Bloom (5) have investigated the use of copper, steel and Monel metal tubes in the production of aromatics from paraffins. Wheeler and Wood (21) noted the similarity between the results obtained when methane is heated to 1050° C. in silica or chrome-iron tubes for a given time

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of contact. These authors did not specify the composition of the alloy used. Later Podbielniak (18), using special alloy steel tubes, the composition of which was not given, reported the results obtained in the course of semi-commercial scale experiments on the conversion of stabilizer and refinery gases into aromatics. In both of the above investigations it was found that the deposition of carbon upon the metals used caused considerable difficulties. In Podbielniak's experiments, for instance, it was found necessary to "blow" the reaction tubes with steam every 8–12 hr. in order to remove the carbon deposit. More recently this author has stated* that nichrome appears to be a more suitable material than the alloys so far investigated for the thermal treatment of hydrocarbons. Porter (19) reports that iron, nickel and similar metals possess a harmful and catalytic influence in the production of benzol by the thermal treatment of refinery gases and are therefore not suitable materials from which to construct reaction tubes. It was found, however, that an iron tube coated with chromium or tin could be used satisfactorily at temperatures of 825–950° C. Harnsberger (14) found that chrome-nickel alloy steels were suitable at 700–760° C. in the production of oil gas by the pyrolysis of petroleum fractions. It was necessary, however, to "blow" the cracking tubes periodically with steam or air in order to remove the deposit of carbon.

Steigerwald (20) in a patent on the conversion of gases containing methane to liquids claims that iron and the special alloy steels, *e.g.*, V2A or WT2, are useless, since they have the effect of promoting the decomposition of the hydrocarbon into carbon black and hydrogen. It is further claimed that heat resistant materials coated with chromium or molybdenum can be used at temperatures of 800–1200° C. Tubes protected in this manner are claimed not to catalyze carbon formation to any greater extent than quartz or porcelain.

Dunstan (7) has reported yields of 23.09% total liquids and 11.65% (=1.6 gal.) of light oil per 1000 cu. ft. of gas put through, in the pyrolysis of propane at 850° C. and atmospheric pressure. Wright (22) states that tubes of the 25-30% chromium alloys are suitable for vapor phase cracking operations when the pressure does not exceed 50 lb. per sq. in. Two vapor phase cracking units using tubes of this alloy and operating at temperatures as high as 870° C. have been in successful operation for over two years.

Foster (8) states that 25-30% chromium alloy tubes have been in use for three years in a vapor phase cracking unit operating at a temperature of 870° C.

Groll (11) has reported the results of experiments in which it was found that copper, iron and nickel tubes were unsuitable for the thermal treatment of gaseous and liquid hydrocarbons as these metals catalyzed the formation of carbon. He reports, however, that chrome-nickel alloy steel tubes of the 18 : 8 type, such as KA2, did not catalyze carbon formation. This latter observation does not agree with conclusions based upon the results of experiments carried out in these laboratories under similar conditions and using chromium-nickel alloy steel tubes of the 18 : 8 type.

*See Reference (9, p. 72).

The commercial development of thermal processes for the production of aromatics by the pyrolysis of the gaseous paraffins or the cracking of liquid hydrocarbons has been considerably retarded on account of the low throughput obtainable in pyrolysis or vapor phase cracking units. This difficulty can be largely overcome by the use of specially designed reaction tubes in which a high degree of turbulence is induced in the gas flow through the reaction chamber. As a result of the marked increase in the rate of heat transfer from tube wall to gas and the more uniform temperature distribution within the reaction space, the writers have shown, in previous communications (2, 3, 4), that the throughput of a given size of reaction tube at a given temperature is almost doubled when the tube is used for the conversion of gaseous paraffins to olefines, and increased by about 50% when the tube is used for the conversion of gaseous paraffins to liquid hydrocarbons. This has made it possible to obtain high rates of conversion at temperatures considerably lower than is the case when open tubes are used.

The purpose of this investigation was to determine the behavior of the chromium-nickel and high chromium heat resistant alloys in the conversion of propane to aromatics. Propane was chosen because this hydrocarbon is readily available and also because the conditions required for its thermal treatment are approximately the same as those required for the thermal treatment of refinery or stabilizer gases.

Materials Used

The propane used in these experiments was obtained from the Carbide and Carbon Chemicals Corporation. The value of n in C_nH_{2n+2} as determined by slow combustion analysis was 2.98.

Apparatus

The apparatus used in all except the pressure experiments was essentially the same as previously described, the furnace being the same as that used in the conversion of paraffins to olefines in metal tubes (3) and the recycling apparatus similar to that employed in the conversion of paraffins to liquids in quartz (4).

Experimental

(A) *Recycling Experiments in KA2S Tubes*

The following experiments were carried out particularly to determine the amount of carbon deposited in a baffled KA2S tube when propane is thermally treated for maximum liquid production. The results obtained are given in Table I. In this and subsequent tables, the letters used as column headings refer to the following data:—

A, total yield of liquids in gm. per hour;

B, percentage by weight of the propane put through recoverable as olefines from the exit gas;

C, percentage conversion to liquids, based on the weight of propane put through;

D, percentage conversion to light oil, based on the weight of propane put through;

E, yield of liquids in lb. per 1000 cu ft. propane put through;

F, yield of light oil in lb. per 1000 cu ft. propane put through;

G, ratio light-oil/tar;

H, carbon formed, gm. per hour.

TABLE I

EXPERIMENTS WITH KA2S AND 28% CHROMIUM NICKEL-FREE BAFFLES (KA2S TUBE)

Expt. no.	Temp., °C.	Gas rate, l/hr.		Duration of run, hr.	Expansion, %	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H**
		In	Recycle										
Baffles of KA2S													
37	917	143	340	1	101	54.6	30.3	19.6	12.9	23.9	15.6	2.0	20.0
38	920	144	289	1	103	68.2	26.9	24.3	15.6	29.6	19.0	1.8	8.0
39	922	144	279	1	100	66.3	—	23.6	14.3	28.8	17.4	1.5	7.0
40	900	143	239	5	99	56.6	31.0	20.3	13.1	24.8	16.0	1.8	7.2
41	900	143	243	2	104	57.4	32.3	20.6	13.7	25.1	16.7	2.0	6.3
Baffles of 28% chromium nickel-free alloys													
42	900	138.5	162	2	103	69.4	—	25.6	14.4	31.3	17.4	1.8	3.1
43	900	139.5	278	2	106	72.0	26.8	26.4	16.8	32.3	20.4	1.6	5.5

**Carbon removed by scraping.*

It will be observed that the amount of carbon deposited per hour dropped considerably after the first experiment, but is, nevertheless, too great to permit the use of 18 : 8 chrome-nickel alloys under the above conditions. It was hoped that, with prolonged use, the activity of the metal would decrease. The above and following experiments show that this effect does not occur, the metal apparently retaining its activity even after 25-30 hours' use. In Experiment 40 the length of time the KA2S baffled tube could be used, before blocking due to deposition of carbon occurred, was found to be about five hours. The necessity of "blowing" the tube with steam or air at frequent intervals, in order to remove the deposit of carbon, makes it doubtful whether the use of this alloy would be practicable.

In Experiments 42 and 43 in which the KA2S baffles were replaced by baffles of 28% chromium nickel-free alloy the carbon formed decreased somewhat, but the difference is too small to permit any conclusions being drawn as to the relative effects of the two alloys.

It was found that the temperature required for the conversion of propane to liquids is appreciably lower in alloy steel tubes than in quartz tubes on account of the higher rate of heat transfer through the metal. Thus in previous

experiments in silica tubes (*cf.* Experiment 33 (4)) it was found that a conversion of 23.8% to liquids was obtained at 942° C., whilst in Experiments 42 and 43 in a metal tube of the same reaction volume, 25.6 and 26.4% conversion were obtained at 900° C.

The analyses of the gaseous products obtained in the above experiments are given in Table II.

TABLE II

ANALYSIS OF GASEOUS PRODUCTS. EXPERIMENTS 37-43

Expt. no.	% by volume			
	C_2H_2	C_2H_4	C_2H_6	H_2
37	2.2	19.0	2.0	29.6
38	2.6	16.8	1.7	31.9
40	2.0	20.3	1.6	28.2
41	2.1	20.6	1.7	28.1
43	2.6	16.6	1.6	31.6

The following series of experiments was carried out to determine whether the catalytic influence of the nickel alloy on carbon formation decreased after prolonged use. The results, which are given in Table III, show that it is very doubtful whether this material would prove suitable for the thermal treatment of paraffin gases as there was no evidence that the catalytic activity of the alloy decreased.

TABLE III

CARBON FORMATION WITH KA2S AND 28% CHROMIUM NICKEL-FREE BAFFLES (KA2S TUBE). TEMP., 900° C.

Expt. no.	Rate, l/hr.		Expansion, %	Duration of run, hr.	Carbon formed, gm.
	In	Recycle			
44	139.5	227	109.5	1	6.1
45	139.5	227	109.5	1	18.0
46	65.0	122	85.0	1	8.5
47	139.0	113.5	121.0	2	8.2
48	104.0	114	94.0	2	2.9
49	141.5	237	97.0	1	5.3
50	139.0	278	98.5	2	8.0
51*	140.0	278	98.0	1	15.0
52*	141.0	278	100.0	1	2.5
53*	139.0	287	95.0	2	0.9

**Baffles of 28% chromium nickel-free alloy.*

Although the above experiments were carried out under apparently similar conditions, for some unknown reason considerable variations were observed in the amounts of carbon formed. The results show, however, that the metal does not lose its catalytic activity with prolonged use.

In the experiments with nickel-free baffles (Experiments 51–53) the carbon was found to deposit almost exclusively on the wall of the tube, the only deposit found on the baffles being a very thin film of the lustrous grey carbon similar to that which forms on an inert surface, such as silica, under similar conditions.

The deposit of fluffy, black, catalytic carbon which was observed to form when the chromium-nickel alloy was used was thought to be due to the presence of nickel in the alloy. This was apparently confirmed when extraction of the carbon with hydrochloric acid gave a solution containing considerable amounts of nickel. The solution was also found to contain iron, but the presence of the latter element was not thought to have any marked effect on carbon deposition until it was observed that the formation of a voluminous deposit of catalytic carbon will also occur in nickel-free alloy tubes containing 20–30% chromium, if these are subjected to pyrolysis conditions for some time, then heated in air at 750–800° C. for removing the carbon film on the surface, and then used again for pyrolysis. When first used for pyrolysis, the surface of the high chromium alloy steel tubes and baffles becomes covered with a hard, gray film of carbon, which grows very slowly. If a tube and baffles are used for pyrolysis at 800° C. for several days, and then air passed through the tube at 750–800° C. for burning off the carbon film, the surface of the alloy becomes covered with a loose, brick-red deposit of oxides, which contain chromium as well as iron. There seems to be little doubt that the formation of this oxide film is responsible for the catalytic activity of the tube in promoting carbon deposition. Similar results have been obtained with KA2S alloy; heating in air after using tubes and baffles of this alloy for pyrolysis at 800–850° C. also results in the formation of a loose oxide film on the surface of the metal, and causes a considerable increase in the rate of carbon deposition under given conditions when the tubes are used again for pyrolysis. Groll (12) has also observed increased carbon deposition in KA2 and high chromium alloy tubes which had been heated in air after being subjected to pyrolysis conditions.

It may be pointed out that the use of baffles in the writers' experiments has made it very convenient to observe the condition of the surface of the metal after each experiment. It appears quite probable that the loss of resistance of the high chromium and of the 18–8 alloys against air oxidation is due to carburization of the alloy under pyrolysis conditions. This conclusion is based on the fact that the iron-chromium ratio of the oxide film in the case of the high chromium alloy is different from that of the alloy itself, and the observation that with the high chromium, as well as with the 18–8 alloy, if direct contact of the metal with the carbon film (which always deposits on the reaction tube and on the baffles during pyrolysis) is prevented by first covering the metal with an inert protective coating, these alloys can be repeatedly used for pyrolysis and heated in air without any oxide film forming on the surface, and without any apparent increase in the rate of carbon deposition.

The following experiments were carried out to determine the effect of increasing the recycle rate and the temperature on the yield of liquids and also to determine the effect of continued use on the deposition of carbon in the KA2S tube. In all of these experiments a tube of KA2S alloy with baffles of 28% chromium nickel-free alloy was used. The results obtained are given in Table IV.

TABLE IV

EXPERIMENTS AT HIGHER TEMPERATURE AND RECYCLE RATE WITH KA2S AND 28% CHROMIUM NICKEL-FREE BAFFLES (KA2S TUBE)

Expt. no.	Temp., °C.	Rate, l/hr.		Expansion, %	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*
		In	Recycle									
54	900	139	411	98	66.9	28.8	24.7	18.3	30.1	22.3	2.9	2.5
55	903	142	546	91.3	49.5	—	17.8	14.5	21.7	17.7	4.5	7.6
56	930	142	546	109	71.0	28.4	25.6	18.7	31.2	22.8	2.7	2.6
57	902	192	427	101	81.7	34.4	21.8	16.3	26.6	19.9	2.9	2.9
58	930	192	448	108	102.7	30.9	27.4	19.1	33.4	23.3	2.3	3.8
59	930	214	377	110	108.5	29.2	25.8	17.3	31.5	21.1	2.0	2.4
60	930	187	450	120	100.1	—	27.4	18.5	33.4	22.6	2.1	2.3

It will be observed that in Experiments 54 and 55, in which the recycle rates were higher than those used in Experiments 40 and 41, the temperature being the same in both cases, the yields of light oil increased, whilst the light-oil/tar ratio was consistently higher, as compared with Experiments 41 and 42. In Experiment 56, in which the temperature was increased to 930° C., the recycle rate being the same as in Experiment 55, the yields of total liquids and light oil and the light-oil/tar ratio were the same as in Experiment 54, in which the temperature used was 900° C. and the recycle rate 411 litres per hour.

In Experiments 57-60, the inlet gas rate was increased, the temperature being raised to 930° C. in Experiments 58-60 and the recycle rate varied between 377 and 450 litres per hour. The optimum conditions appear to be those of Experiments 58 and 60, which gave a yield of total liquids of over 100 gm. per hr., the yield of light oil being equivalent to 23.3 lb. (2.7 gal.) per 1000 cu. ft. of propane put through. It will also be observed that the light-oil/tar ratio of the liquids obtained at the higher recycle rate is appreciably higher than in the previous experiments at lower recycle rates and lower temperature. The improved results obtained on increasing the recycle rate are undoubtedly due in part to the increasing effect of turbulence at the higher gas velocities.

TABLE V

ANALYSES OF GASEOUS PRODUCTS. EXPERIMENTS 54-59

Expt. no.	% by volume					*n* for residue
	C_2H_2	C_2H_4	C_3H_6	H_2	Residue	
54	2.2	19.5	1.2	29.4	47.7	1.03
56	2.7	18.6	0.8	31.1	46.8	1.01
57	2.3	21.9	2.1	27.1	46.6	1.00
58	2.9	17.2	2.9	30.5	47.5	1.07
59	2.9	17.6	1.8	31.1	46.6	1.02

The analyses of the gaseous products obtained are given in Table V.

(B) *Recycling Experiments in 28% Chromium Nickel-free Alloy Tubes*

In the following experiments the pyrolysis of propane to liquids was carried out in a tube of nickel-free 28% chromium alloy in order to compare the

behavior of this alloy, as regards carbon formation, with the KA2S alloy previously used. Owing to the relatively high creep rate of the 28% chromium alloy at temperatures above 850° C. the temperature was kept at or below this point. The results are given in Table VI.

TABLE VI

EXPERIMENTS WITH TUBE AND BAFFLES OF 28% CHROMIUM NICKEL-FREE ALLOY

Expt. no.	Temp., °C.	Rate, l/hr.		Expansion, %	*A*	*B*	*C*	*D*	*E*	*F*	*G*
		In	Recycle								
Pyrolysis in 85-cm. furnace											
61	835	219	232	87.0	32.4	49.0	7.0	5.6	9.2	6.8	—
62	840	211	237	98.5	41.3	53.9	11.0	8.4	12.2	10.2	—
63	850	212	230	98.5	47.6	46.8	11.5	9.1	14.0	11.1	3.7
64	833	208	228	94.0	37.1	49.2	9.1	—	11.0	—	—
Pyrolysis in 140-cm. furnace											
65	810	210	220	95.5	39.3	45.8	9.6	8.5	11.7	10.4	8.0
66	830	210	234	97.5	63.0	41.2	14.1	10.2	17.2	12.4	4.6
67	850	204	238	106	80.7	38.4	20.2	15.4	24.6	18.8	3.2
68	850	153	323	105	65.7	34.0	21.4	16.0	26.2	19.6	2.7
69	850	280	134	109	114.5	39.8	20.9	—	25.5	—	—

The analyses of the gaseous products from these experiments are given in Table VII.

TABLE VII

ANALYSES OF GASEOUS PRODUCTS. EXPERIMENTS 61-69

Expt. no.	% by volume					*n* for residue
	C_2H_2	C_2H_4	C_3H_8	H_2	Residue	
61	0.6	26.7	7.7	19.8	45.2	1.20
62	1.0	27.6	8.0	19.5	43.9	1.16
63	1.7	29.0	3.6	22.2	43.5	1.03
64	0.0	27.9	6.0	18.8	47.3	1.20
65	0.7	24.8	3.4	18.3	52.8	—
66	0.7	24.0	4.3	20.2	50.8	—
67	1.4	24.7	1.7	22.2	50.0	1.00
68	1.3	22.5	1.1	24.1	51.0	—
69	0.4	25.3	1.7	25.4	47.2	—

In these experiments the amount of carbon deposited was practically negligible. A thin film of the hard, gray variety of carbon deposited on the tube wall and baffles. The rate of growth of the film, as determined by measuring its thickness after the reaction tube had been used for several hours, appears to be of the order of 0.007 mm. per hour at 850° C.

In Experiments 61–64 in which the length of the furnace was 85 cm. the maximum yield of liquids was 11.5% at 850° C. In order to increase the percentage conversion to liquids without raising the temperature, the heated length of the furnace was increased to 140 cm. by adding another section. The maximum percentage conversion of propane to liquids in the longer furnace was over 20% at a temperature of 850° C.

The yields of liquid and the throughput of the 140 cm. furnace could be increased by operating at a higher temperature or by further increasing the length of the furnace. Several limiting factors, however, prevented the carrying out of these experiments under more favorable conditions. The appreciable creep rate of the alloy used, when the latter is subjected to a temperature above 850° C., did not permit raising the temperature above that point, and made it impractical to increase the length of the furnace beyond the present dimension.

(C) *Recycling Experiments under Pressure in the 28% Chromium Alloy Tube*

The conversion of propane to liquids takes place in two distinct steps, (i) the cracking of the paraffin to olefines and (ii) the polymerization of the olefines to liquids. At atmospheric pressure and the temperatures used in the present experiments, the reaction involved in the first step takes place at a greater rate than the polymerization reaction. It was thought that increase

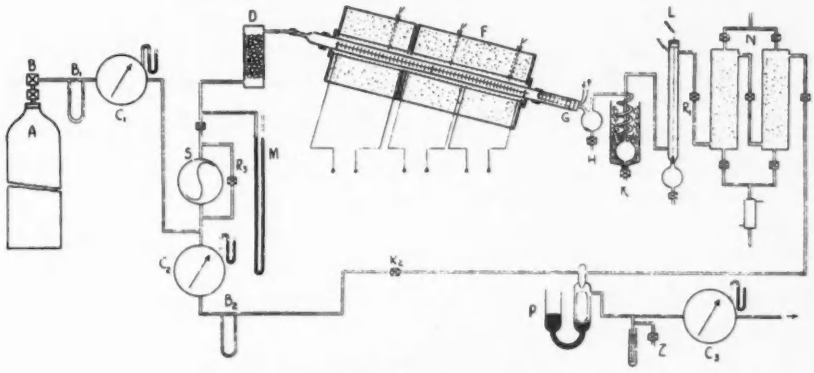

FIG. 1. *Apparatus used in pressure experiments.*

in pressure would, within limits, cause an increase in the rate of polymerization of the olefines without appreciably affecting the rate of cracking of the paraffin.

The following experiments were carried out to determine the effect of increasing the pressure up to one atmosphere on the conversion of propane to liquids.

The apparatus used is shown in Fig. 1. Gas was passed from the cylinder *A* through the low pressure valve *B*, the flowmeter B_1, the wetmeter C_1, the pump *S*, the calcium chloride tower *D* and the furnace *F*. The exit end of the reaction tube was cooled by means of the water cooled copper tube carrying baffles *G*. Most of the heavy tar in the exit gas separated out in *H* and a considerable amount of the lower boiling constituents collected in the condenser *K*, from which the gas passed to the Cottrell precipitator *L* and through the valve R_1 to the charcoal absorbers *N* which retained the butadiene, benzene and higher aromatics. The scrubbed gas then passed through the

three-way valve P from which a portion was recycled to the furnace through the flowmeter B_2, the wetmeter C_2 and the pump S, the remainder being vented to the hood through the wetmeter C_3. The pressure in the reaction chamber could be controlled by adjusting the valves R_1 and R_3. By adjusting the valve R_2, the desired fraction of the exit gas from the absorbers could be vented through the valve P or recycled through the pump S. The pressure of the gas in the reaction chamber was measured by the mercury manometer M. Samples of the vented gas were taken for analysis at Z.

All experiments were carried out in a 28% chromium alloy steel tube of 2.5 cm. internal diameter with baffles of the same material. The heated length of the tube was 85 cm. in Experiment 71 and 140 cm. in the other experiments. The results obtained are shown in Table VIII.

TABLE VIII

RECYCLE EXPERIMENTS AT PRESSURES HIGHER THAN ONE ATMOSPHERE

Expt. no.	Temp., ° C.	Rate, l/hr.		Pressure, cm. Hg.	Expansion, %	*A*	*B*	*C*	*D*	*E*	*F*	*G*
		In	Recycle									
70	820	229	350	54	102	110.7	31.5	24.8	16.3	30.3	19.9	1.9
71*	810	232	334	47	96	97.2	34.0	21.4	17.0	26.2	20.8	3.7
72	800	229	388	74	98	125.2	27.1	28.0	19.1	34.2	23.3	2.1
73	800	276	413	72.5	97	111.5	—	20.7	16.8	25.3	20.5	4.4
74	810	276	387	73.5	99	127.4	33.2	23.6	17.4	28.8	21.2	2.8

*85 cm. furnace.

The analyses of the gaseous products obtained in certain of the above experiments are given in Table IX.

TABLE IX

ANALYSES OF GASEOUS PRODUCTS. EXPERIMENTS 70-74

Expt. no.	% by volume				
	C_2H_2	C_2H_4	C_3H_6	H_2	Residue
70	1.5	21.9	1.6	24.7	50.3
71	0.5	23.6	2.5	19.4	54.0
72	0.5	19.8	1.1	20.6	58.0
74	0.6	23.1	2.0	19.4	54.9

It will be observed that increasing the pressure up to about one atmosphere has a very marked effect on the rate of formation of liquids. Yields of light oil of over 20 lb. per 1000 cu. ft. were obtained in Experiments 72 and 74 at pressures of about 73 cm.

The effect of pressure is well illustrated by comparison of the results of the above experiments with those obtained when the pressure was atmospheric.

Thus, for instance, in Experiment 67 (Table VI) a yield of light oil of 18.8% was obtained at a temperature of 850° C., whilst in the above experiments yields of 23.3% at 800° C. and 21.2% at 810° C. were obtained although the inlet gas rate was appreciably higher. One would consequently expect

that the use of still higher pressures would cause a further reduction of the temperature required for the same rate of conversion, or, if the 28% chromium tubes can be used continuously at 800–810° C., an increase in the throughput of a reaction tube of a given size at that temperature.

It was expected that increase in pressure would tend to increase carbon deposition in the tube, but the present experiments have shown that there is no appreciable increase in the amount of carbon deposited when the pressure is increased to one atmosphere.

(D) *Composition of Gaseous and Liquid Products*

(1) *Gaseous Products*

Ethylene. It has been observed that when propane is thermally treated under what appear to be the optimum conditions for the production of aromatics, about 30% by weight of the propane is converted to olefines, mostly ethylene.

It is therefore obvious that the production of aromatics by the above process would have much greater commercial possibilities if the considerable amounts of olefines obtained as by-product could be profitably utilized for the production of such chemicals as ethyl alcohol or ethylene glycol. Under these conditions the total conversion to useful products (olefines plus aromatics) in the pressure experiments would be about 55%.

Butadiene. In steaming out the charcoal absorbers the vapors were passed through a condenser kept at 15° C. to condense the benzene and higher boiling constituents. The remaining gas which consisted mainly of butadiene, with smaller amounts of mono-olefines, was passed upwards through a water jacketed column filled with glass beads down which a 10% solution of bromine in carbon tetrachloride was passed. It was found that unless the solution of the bromides was allowed to stand for some time in contact with excess bromine, the conversion of the butadiene to the tetrabromide was not complete, considerable amounts of α, δ,-dibrombutene-2 being present. The solid and liquid isomers of this compound were separated in several experiments in which insufficient excess of bromine had been used.

The light oil recovered from the absorber contains some dissolved butadiene. In order to recover the butadiene dissolved in this oil, the latter was gently refluxed under a condenser cooled to 10-15°C. until the evolution of gas subsided, the evolved vapors brominated as before and the solution of bromides added to the main bulk which was then freed from excess bromine and dried. Most of the carbon tetrachloride was removed on the water bath and the residue fractionated under reduced pressure. The distillate up to 80°C./20 mm. was found to consist of ethylene and propylene dibromides. There was very little distillate between 80°C./20 mm. and 130°C./20 mm. At this point it was found that the residue in the flask partly solidified on cooling and on dissolving in hot 95% ethyl alcohol and allowing to cool, crystals of the high melting isomer of butadiene tetrabromide (m.p. 118°C. corr.) were deposited. The lower melting isomer was separated as a heavy oil from the residual

alcoholic solution by removing the alcohol *in vacuo*. The oil crystallized completely on cooling to 0° C. and after recrystallizing from 95% ethyl alcohol (in which the compound is very soluble) the crystals melted sharply at 37° C. The two isomers appeared to be produced in equal amounts which agrees with statements in the literature (10, 16). Since the tetrabromides were the only compounds remaining after fractionation of the mixed bromides to 130° C./20 mm., the amount of butadiene formed could be estimated accurately by weighing the tetrabromide residue.

Table X shows the yield of butadiene obtained in various experiments in which propane was thermally treated for the production of liquids in a tube of the 28% chromium alloy, and in which the butadiene formed was converted quantitatively to the tetrabromides.

TABLE X

YIELD OF BUTADIENE FROM PROPANE

Expt. no.	Temp., ° C.	Rate, l/hr.		Furnace dimensions	% C_4H_6, based on weight of C_3H_8 passed
		In	Recycle		
63	850	212	230	85 by 2.5 cm.	5.0
64	834	208	228	85 by 2.5 cm.	4.4
67	850	204	238	140 by 2.5 cm.	4.9

(2) *Light Oil (boiling below 200° C.)*

After the removal of butadiene and dissolved gases, the light oil was fractionally distilled in an electrically heated column filled with an efficient bronze gauze packing. Preliminary investigation showed that the main constituents of the light oil were cyclopentadiene, benzene, toluene, styrene and indene, along with small quantities of unsaturateds boiling up to 130° C., and possibly some tri- and tetramethylbenzenes. The curves obtained in fractionation of typical light oils obtained in the above experiments are given in Fig. 2.

It will be seen that the column employed gave sharp separation of the first three main constituents, the amounts of distillate obtained between the boiling points of these constituents being small. In the case of the styrene-xylene fraction however no sharp cuts could be obtained, but this fraction has been shown to consist largely of styrene.

The first or cyclopentadiene fraction was found to contain about 30% of cyclopentadiene together with smaller amounts of unsaturateds boiling up to 75° C., whilst the percentage of aromatics in the benzene and toluene fraction was over 95%. The styrene fraction has been shown to contain 70–80% of styrene whilst the remainder of the light oil distilling up to 200° C. contained about 70% of indene.

Cyclopentadiene fraction (25 to 78° C.). Cyclopentadiene was present in considerable amounts in the fraction boiling at 35–45° C. and was identified and gravimetrically determined by conversion to *cis*endomethylene 3,6-tetra-

hydrophthalic anhydride (m.p. 164.6° C. corr.) by reaction with maleic anhydride (1, 6). The fraction boiling between 45° and 75° C. was found to be highly unsaturated. The nature of the compounds present in this fraction was not investigated but it is probable that hexadienes and methylcyclopentadiene were present. In most cases the amount of cyclopentadiene in the total fraction was about 30% by weight. The presence of cyclopentadiene in the light oil obtained in the thermal treatment of the lower paraffins has been reported by Frey and Hepp (10), who also obtained indications of the presence of pentenes, hexadienes and methylcyclopentadiene in this fraction.

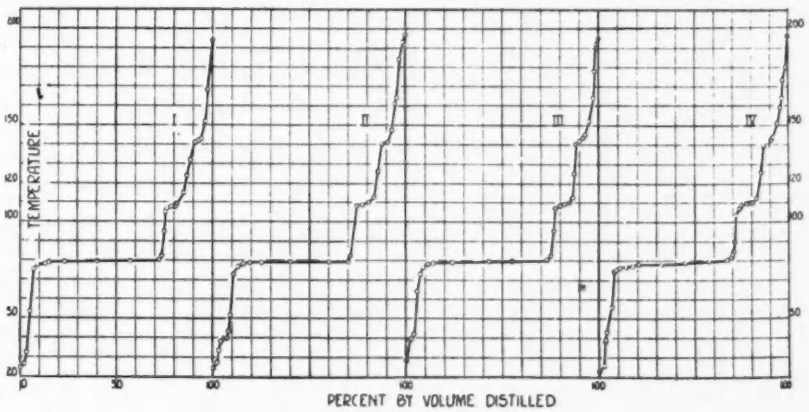

FIG. 2. *Distillation curves of light oils.*

Benzene fraction (78.0–82.0° C.). The fraction boiling at 75.1–78.8° C. contained small amounts of non-aromatics. This is shown by the iodine absorption value and also by the shape of the distillation curve at this point. Low temperature bromination of the fraction boiling at 75.1–78.8° C. and removal of the benzene present gave an unstable dark colored oil which evolved hydrobromic acid on warming. This behavior is characteristic of cyclohexene dibromide and it is likely that this material was present in this fraction since its presence has been reported in light oils of similar origin. The iodine number of this cut was not appreciably lowered by refluxing with maleic anhydride and distilling. Hence diolefines were probably absent. Assuming that the iodine absorption was due to the presence of cyclohexene, the amount of this material present would be 0.7% by weight of the total benzene fraction. These results show that the benzene fraction is practically free from gum forming constituents.

Table XI shows the distillation range, iodine absorption numbers (in centigrams of iodine per gram of material) and percentage of total oil distilling in the benzene range, the results being obtained on fractionation of a light oil produced by the pyrolysis of propane for the production of aromatics under the conditions described above.

Toluene fraction (82.0–126.0° C.). The cut boiling between 105 and 111° C. consisted chiefly of toluene which was identified by the preparation of the 2,4-dinitro derivative (m.p. 71.5° corr.) and comparison (mixed melting point) with an authentic specimen. The color of this fraction was pale yellow and the presence of a certain amount of unsaturation was shown by the iodine absorption values of the toluene fractions obtained from several samples of light oil. These together with the percentage yield of this fraction are given in Table XII.

TABLE XI

IODINE NUMBERS OF CUTS IN THE BENZENE FRACTION

Temp. range, ° C.	Iodine number, cgm. iodine/gm.	% by weight of cut based on total light oil
75.1–78.8	19.9	7.2
78.8–79.8	1.7	25.6
79.8–80.8	1.0	27.0
80.8–82.0	2.5	11.2

TABLE XII

IODINE NUMBERS AND YIELDS OF TOLUENE FRACTIONS

Expt. no.	Temp., ° C.	Rate, l./hr.		Furnace dimensions, cm.	Iodine no., cgm. iodine/gm.	% by weight of fraction based on total light oil
		In	Recycle			
	850	210	228.5	2.5 by 85*	14.7	11.5
65	810	210	220	2.5 by 140	11.4	13.1
68	850	153	323	2.5 by 140	11.4	11.3
71	810	232	334†	2.5 by 85	16.0	13.9
72	800	229	388‡	2.5 by 140	13.2	11.1

**KA2S tube, all other experiments with 28% chromium alloy tube. †Pressure, 47 cm. Hg. ‡Pressure, 74 cm. Hg.*

Xylene fraction (126.0–164.0° C.). Most of the fraction boiling between 126 and 164° C. was found to distil in the range 135–145° C. When freshly distilled the color of this fraction is pale yellow, but darkens somewhat on exposure to light; on standing at room temperature for several weeks the fraction becomes exceedingly viscous. This fraction was highly unsaturated as shown by its high iodine absorption value. The presence of styrene in liquids obtained under similar conditions has been reported by other investigators (10, 11). Bromination of the xylene fraction of the light oil showed that it consisted mainly of styrene. There did not appear to be any other unsaturated compounds present in more than traces, since the residue of crude styrene dibromide had a melting point only slightly lower than that of the pure compound. After one recrystallization from 95% ethyl alcohol the dibromide melted at 73° C. (corr.). Hence it was possible to obtain a fairly accurate value for the amount of styrene present by means of the iodine absorption numbers and by direct bromination.

Owing to the importance of styrene as a raw material for the manufacture of synthetic resins, its presence in appreciable amounts in the light oil obtained

by the thermal treatment of propane is of interest. Table XIII shows the amounts of the fraction boiling at 126–164° C. as percentage of the total light oil, the percentage of styrene in that fraction and the yield of styrene based on propane put through. The styrene was determined by direct bromination and weighing the dibromide formed or by calculation from the iodine number. It will be seen that in most experiments the amount of styrene present was equal to over 70% of the total fraction.

TABLE XIII

YIELDS OF STYRENE IN THE PYROLYSIS OF PROPANE TO AROMATICS

Temp., ° C.	Rate, l./hr.		Furnace dimensions, cm.	Iodine no., cgm. iodine/gm.	Yield 126-164° C. fraction, % total light oil	% Styrene in 126-164° C. fraction	Yield styrene, as % propane passed
	In	Recycle					
840	211	237	2.5 by 85	175.9	7.9	72	0.58
850	210	228.5	2.5 by 85*	164.8	8.3	67	0.59
850	212	230	2.5 by 85	178.2	9.4	73	0.64
810	210	220	2.5 by 140	178.8	11.0	74	0.69
850	153	323	2.5 by 140	209	8.3	86	1.14
810	232	334†	2.5 by 140	183	7.7	75	1.00
800	229	388‡	2.5 by 140	197	6.6	80	1.01

**KA2S tube, all other experiments with 28% chromium alloy. †Pressure, 47 cm. Hg. ‡Pressure, 74 cm. Hg.*

On brominating a quantity of this fraction (50 gm.) collected in several experiments and distilling under reduced pressure, a small amount (6 gm.) of distillate was obtained which did not react with bromine and distilled in the range 130–145° C./760 mm. The amount was too small to permit an accurate fractionation being effected, but by distilling through a small bronze-packed column and collecting the portion distilling at 135–139° C., followed by strong nitration, *p*- and *m*-trinitroxylenes were obtained, the identities of which were confirmed by taking mixed melting points with authentic specimens.

Fraction boiling at 150–169° C. The small fraction obtained in this range was highly unsaturated. By applying the method used in separating the xylenes to a composite sample collected in several experiments, a few drops of liquid were obtained which on strong nitration gave a derivative having a constant melting point of 182° C. (corr.) after repeated recrystallization from 95% ethyl alcohol. This is only slightly below the recorded melting point of trinitropseudocumene and it is, therefore, likely that pseudocumene was present in small amounts.

Fraction boiling at 169–185° C. This fraction was also highly unsaturated, reacting with a well cooled solution of bromine in chloroform to give, on evaporation of the chloroform, a pale yellow oil that slowly crystallized on strong cooling. Indene was identified both by the properties of the dibromide

TABLE XIV

PERCENTAGE YIELDS OF MAIN FRACTIONS OF LIGHT OILS

Expt. no.	Temp., ° C.	Rate, l./hr.		Furnace	Main fractions, % by wt. of light oil					Main fractions, % by wt. of propane passed				
		In	Recycle		Cyclopentadiene*	Benzene †	Toluene ‡	Styrene **	Indene ***	Cyclopentadiene	Benzene	Toluene	Styrene	Indene
58 59	930 † 930	192 214	448 377	85 by 2.5 cm., KA2S alloy	7.1	71.0	9.5	8.0	4.4	1.3	12.9	1.8	1.5	0.8
61	835	219	232	85 by 2.5 cm., 28% Cr alloy	22.3	47.4	13.2	11.6	5.5	1.2	2.8	0.7	0.6	0.3
62	840	211	237	85 by 2.5 cm., 28% Cr alloy	17.9	54.3	14.8	9.2	3.8	1.5	4.6	1.2	0.8	0.3
63	850	212	230	85 by 2.5 cm., 28% Cr alloy	11.8	55.8	15.3	11.4	5.7	1.1	5.1	1.4	1.0	0.5
65	810	210	220	140 by 2.5 cm., 28% Cr alloy	20.1	48.3	15.1	12.7	3.8	1.7	4.1	1.3	1.1	0.3
68	850	153	323	140 by 2.5 cm., 28% Cr alloy	9.7	62.4	12.3	12.5	3.1	1.5	10.0	2.0	2.0	0.5
71	810	232	334	140 by 2.5 cm., 28% Cr alloy. Pressure, 47 cm. Hg	11.9	57.6	14.3	10.5	5.7	2.0	9.8	2.4	1.8	1.0
72	800	229	388	140 by 2.5 cm., 28% Cr alloy. Pressure, 47 cm. Hg	8.6	65.1	12.3	10.8	3.2	0.6	12.4	2.4	2.1	0.6
74	810	276	387	140 by 2.5 cm., 28% Cr alloy. Pressure, 73.5 cm. Hg	6.1	63.0	15.7	11.4	3.8	1.1	10.9	2.7	2.0	0.7

*Composite sample fractionated. †Containing about 30% cyclopentadiene. ‡Aromatics above 95%. **Styrene 70-80%. ***Indene about 70%.

produced (m.p. 44° C.) and also by preparing the bromhydrin according to the method of Krämer and Spilker (15). These authors give the melting point of this compound as 130–131° C. (corr.?). The writers' compound after three recrystallizations from boiling water melted at 129.6° C. (corr.).

Estimation of the amount of indene in this fraction by direct bromination and weighing of the dibromide gave figures closely approximating those calculated from the iodine numbers. This would indicate that, except for traces of other olefines which were not identified, indene is the only unsaturated present.

Fraction boiling at 185–200° C. The amount of material distilling in this range was extremely small. Between 195–200° C. the distillate partly solidified on cooling. It possessed an odor resembling naphthalene, but it is not unlikely that higher methylated benzenes are present in small amounts. Beyond proving the presence of naphthalene in this fraction, its composition was not investigated further.

Table XIV shows the proportions of the main constituents for a series of light oils produced in the pyrolysis of propane in metal tubes. Experiments 61, 103, 104 and 105 were carried out mainly for the purpose of producing olefines with relatively low conversions to liquids.

(3) *Tar (boiling above 200° C.)*

Table XV shows the results obtained when a quantity of tar from the recycling experiments was fractionated under a pressure of 13 mm. in a 60-cm. bronze-packed column.

TABLE XV

RESULTS OF FRACTIONATION OF RECYCLE TAR

Temp., ° C./13 mm.	Main constituents	Yield, % by weight	
		Tar	Propane passed
65–97	Probably higher alkyl benzenes	4.5	0.4
97–113	Naphthalene	25.0	2.5
113–133	Methylnaphthalenes	3.1	0.3
133–146	Dimethyl naphthalenes		
146–170	Acenaphthene	6.5	0.7
170–186	Phenanthrene	5.0	0.5
186–215	Phenanthrene		
	Anthracene	12.7	1.3
215–250	Probably methyl and dimethyl anthracenes	13.7	1.4
Above 250		29.5	2.9

Fraction boiling at 65–95° C./13 mm. This fraction was liquid at ordinary temperatures, but deposited a small amount of naphthalene on cooling to zero. Its composition was not investigated.

Naphthalene fraction; 97-113° C./13 mm. The fraction solidified completely on cooling and had a melting point only slightly lower than that of naphthalene. After one recrystallization from ethyl alcohol it melted at 80° C. and gave a picrate melting at 152° C. (corr.).

Methylnaphthalene fraction; 113–133° C./13 mm. On refractionation of the liquid fraction boiling at 113–133° C./13 mm. most of the fraction distilled at 235–245° C./760 mm. This suggests the presence of monomethylnaphthalenes. The fraction boiling at 239–242° C./760 mm., obtained on redistilling, solidified partly when cooled to −12° C. and gave a picrate melting at 116.5° C. which showed no depression of the melting point when mixed with an authentic sample of the picrate of the β-compound. The melting points of the picrates of the α- and β-compounds are 141° and 115° C. respectively. This would indicate that the fraction consists predominantly of the β-substituted methylnaphthalene.

In view of some recent work by Mayer and Schiffner (17), who found that α-methylnaphthalene was rapidly converted into the β-isomer over silica gel at 450° C., one may assume that, even in the absence of a catalyst, this reaction would be sufficiently rapid at 800–810° C. to convert any α-methylnaphthalene into the β-compound. This would explain why the α-methyl derivative, although undoubtedly formed under the conditions of these experiments, is not present in this fraction.

Dimethylnaphthalene fraction; 133–170° C./13 mm. This fraction gave a considerable amount of distillate at 260–270° C./760 mm. on refractionation. This yielded a picrate melting at 143.3° C. (corr.). On cooling to zero the fraction deposited crystals which were obtained as fine needles (m.p. 95.2° C. corr.) on recrystallization from ethyl alcohol. This compound was proved to be acenaphthene by the preparation of the picrate (m.p. 164.2° C. corr.) and of 4-bromoacenaphthene (m.p. 50° C. corr.) and by comparison (mixed melting points) with authentic samples of these compounds. The relative amounts of dimethylnaphthalenes and acenaphthene were not determined.

Phenanthrene-anthracene fraction; 170–215° C./13 mm. Repeated extraction of this fraction with hot ethyl alcohol gave a residue which crystallized in small leaflets from a large excess of ethyl alcohol and melted at 214° C. and which on oxidation with chromic acid gave anthraquinone (m.p. 285° C.). Phenanthrene was identified by treating an alcoholic extract of the fraction with picric acid. The picrate of anthracene is readily decomposed by alcohol, whereas that of phenanthrene is stable under these conditions. The picrate obtained melted at 144.2° C. and on decomposition with ammonia gave phenanthrene (m.p. 98° C.).

Fraction boiling above 215° C./13 mm. The fraction boiling at 217–232° C./13 mm. was a fluorescent liquid. At 234° C./13 mm. the distillate began to crystallize and the boiling point was constant at 234–235° C./13 mm. The temperature then rose rapidly to 244–246° C./13 mm., in which range a further quantity of distillate which solidified on cooling was obtained. These fractions were not investigated further.

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CHEMICAL INVESTIGATION OF THE CORMS OF *ARISAEMA TRIPHYLLUM* (L.) SCHOTT[1]

By Léo Marion[2]

Abstract

The dried and ground corms lost 5% of their weight when extracted with petroleum ether, and a further 0.9% on subsequent extraction with methanol. Besides a trace of an essential oil, the methanol extract yielded water-soluble and water-insoluble portions. The former contained an acid, $C_6H_8O_5$, m.p. 184° C.; *i*-inositol, $C_6H_6(OH)_6$, m.p. 224° C.; a sugar forming phenylglucosazone; and a crystalline substance, ($C_6H_{10}O_6$ or $C_7H_{12}O_7$), m.p. 120° C., exhibiting the properties of a lactone. In the water-insoluble portion combined with the petroleum ether extract, the following substances have been found present: myricyl alcohol, $C_{30}H_{62}O$, m.p. 82-83° C.; a new sterol, arisaesterol, $C_{36}H_{64}O_2$, m.p. 135° C.; phytosterolin, $C_{31}H_{52}O_6$, m.p. 297° C.; and a mixture of fatty acids.

Arisaema triphyllum (L.) Schott is a low perennial herb belonging to the family Araceae. It grows in eastern North America where it is known by the common name of Jack-in-the-pulpit, and although widely scattered, does not seem to occur very plentifully in any locality. Its tuberous root, or corm, contains an acrid juice which, when applied to the tongue causes, after a few minutes, a burning taste quickly becoming intolerable, and softening down gradually. It has been stated by Barnes (2) that this action on the mucous membrane is probably due to the rhaphides contained in the liquid, and that the juice after filtration had lost this property. But this seems doubtful, especially in view of the known fact that the corms, which are farinaceous, are used by the Indians as food; boiling in water or drying being reported sufficient to remove the acridity associating with the fresh plant, and render it edible.

Some work is extant on two species,—*Arum maculatum* L., and *Arum italicum* Mill. These seem to possess properties very similar to those exhibited by *A. triphyllum*. According to Hébert and Heim (4) *A. maculatum* contains a saponin in quantities seemingly not exceeding 1% of the weight of the fresh plant. This saponin, however, was not obtained in a crystalline condition nor studied beyond ascertaining that on hydrolysis, it yields an insoluble product and a reducing sugar (3). The juice permeating the corms is stated by the same authors to contain a liquid alkaloid closely related to coniceine, or to a homologous base. Although all parts of the plant are said to contain this alkaloid, the quantity present is extremely small (0.005% of the fresh plant). Practically the same has been recorded concerning *A. italicum* (7).

Owing to the interesting properties of *A. triphyllum* and the absence of information concerning it, together with the scanty nature of that relating to *A. maculatum* and *A. italicum*, it was deemed desirable to undertake the chemical investigation of the corms.

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It has not been possible to detect the presence of any alkaloid in the plant, nor of a saponin or any glycosidic product.

Efforts to detect another substance to which the acrid property of the fresh plant might be attributed also failed. That this property might be due to a very volatile product appears extremely doubtful; no evidence of the presence of such a substance was found on cautiously drying the ground corms at 60° C. It therefore seems more probable that the acridity might be due to some compound which is destroyed by heat.

Crystalline *i*-inositol $C_6H_6(OH)_6$, m.p. 224° C.*, was isolated in small amount. The plant extract has also yielded an acidic substance, $C_5H_8O_5$, m.p. 184° C., which, although isomeric, does not seem to be identical with the hydroxyglutaric acids. A further crystalline product having the composition and some of the properties of a sugar-acid lactone was also obtained, but it is neither *d*- nor *l*-allonolactone. This was ascertained by comparison with authentic specimens kindly supplied by Dr. P. A. Levene of the Rockefeller Institute, and Professor W. C. Austin, of the Loyola University School of Medicine, to whom the author acknowledges his indebtedness. Its composition agrees with $C_6H_{10}O_6$, although $C_7H_{12}O_7$ is not excluded.

Besides a sterol, a sterolin and myricyl alcohol, $C_{30}H_{62}O$, the extract was also found to contain a sugar which forms phenylglucosazone and various fatty acids. On account of the difficulty experienced in collecting sufficient material and the remarkably low percentage of the plant extracted by methanol, the quantities of the various products isolated were so small that a more detailed study was not possible. It is proposed to continue the investigation when more material becomes available.

Experimental

The material used in this investigation was collected in the Gatineau Hills and in the neighborhood of Mount Shepherd, in the province of Quebec. It consisted of the corms only, and, when dried, amounted to three kilograms. After washing rapidly with running water, the corms were sliced and dried in an oven at 60° C. in a blast of air. The dried product was then ground to a powder and extracted in Soxhlets, first with light petroleum and then with methanol. Petroleum ether removed 5.0%, methanol, 0.9%; the total extract being 5.9%. After removal of the greater part of the solvent from the methanolic extract, the residue was diluted with water.

Distillation of the Extract with Steam

The entire methanolic extract was subjected to distillation for several hours in a strong current of steam, and the distillate extracted with ether. After washing, drying and removal of the ether, the extract consisted of a small quantity of brown oil, but this was too small to allow further investigation.

**All melting points are corrected.*

Non-volatile Constituents of the Extract

After removal of the volatile constituents with steam, there remained in the distillation flask a dark-brown liquid *(A)* in which was suspended a quantity of dark, soft, resinous material *(B)*. The latter was separated by filtration through a layer of charcoal, washed with water and kept for further examination.

The Aqueous Liquid (A)

The aqueous liquid was reduced by distillation under diminished pressure to a volume of about one litre, and repeatedly extracted with ether (12 to 15 extractions). The extract, washed and dried, yielded only a small quantity of gummy material from which nothing definite could be obtained.

Isolation of an Acid

After further evaporation under reduced pressure to a volume of about 800 cc. the aqueous solution was heated to boiling and repeatedly shaken with hot amyl alcohol. The amyl alcohol was removed from the extract by distillation *in vacuo* and, finally, after addition of a little water, by steam distillation. Water was removed under reduced pressure from the residual solution, and the resulting syrup dissolved in ethyl acetate, the filtered solution being poured into ten times its volume of ether. This precipitated a gummy substance from which the supernatant liquor was decanted and evaporated to a small volume. The latter on standing, deposited a small quantity of acicular crystals which were recrystallized from benzene containing a little methanol, m.p. 183-184° C. From a solution of the precipitate in methanol (charcoal), a further crop of the same crystalline substance was obtained. Calcd. for $C_5H_8O_5$: C, 40.54; H, 5.45%; M.W. 148. Found: C, 40.97, 40.67; H, 5.31, 5.27%; M.W. 145, 147 (Rast). The product is acidic and is removed from its amyl alcoholic solution by aqueous potassium carbonate. A review of the literature failed to reveal any record of a substance of this composition, having identical properties.

To the aqueous solution, which had been extracted with amyl alcohol and freed of this solvent by distillation in a current of steam, a hot solution of basic lead acetate was added as long as a precipitate formed. This was filtered and washed by decantation with hot water. The combined filtrate and washings were deleaded with hydrogen sulphide and evaporated under diminished pressure to a syrup. Methanol was then added and the filtered solution again evaporated, the operation being repeated several times to remove the inorganic material. A small portion of the final residue, dissolved in water, and treated with phenylhydrazine yielded phenylglucosazone, m.p. 201° C. The main portion of the residue, dissolved in methanol and allowed to stand for several days, failed to yield anything crystalline. The solution was then evaporated and the residue boiled for five minutes in 5% aqueous sodium hydroxide, cooled rapidly and extracted with ether. This ethereal solution was shaken with 5% aqueous solutions of ammonium carbonate, potassium carbonate and sodium hydroxide, but failed to yield anything crystalline, and was discarded.

Isolation of i-Inositol, $C_6H_6(OH)_6$

The basic lead acetate precipitate was suspended in water and decomposed with hydrogen sulphide led into the vigorously stirred suspension. The precipitated lead sulphide was filtered, the filtrate distilled under reduced pressure to a thick syrup which was dissolved in methanol, and the solution allowed to stand at room temperature for several days. Small, transparent, prismatic needles were gradually deposited which, after several recrystallizations (charcoal) from methanol, melted at 223-224° C. This crystalline substance is very soluble in water, soluble in alcohol, but insoluble in ether. The salmon color produced by inositol in Scherer's test (6) was obtained with this substance. Calcd. for $C_6H_{12}O_6$: C, 40.00; H, 6.67%. Found: C, 40.11; 40.08; H, 6.83, 6.75%. Admixed with a known sample of *i*-inositol, the melting point was unchanged. The presence of *i*-inositol in the plant extract is, therefore, established.

Isolation of an Unidentified Substance

The methanolic mother liquor from the crystallization of *i*-inositol, when allowed to evaporate further, spontaneously deposited transparent, flat, elongated plates which, recrystallized from methanol or water, softened at 105° C. and melted completely at 120° C. The product is inert towards Fehling's solution but when reduced with sodium amalgam at 0° C. in a solution kept slightly acid with sulphuric acid, its power for reducing Fehling's solution gradually increases as the reaction proceeds. *d*-Allonolactone, prepared by Levene and Jacobs (5), has a similar percentage composition, identical melting point characteristics and behaves similarly towards Fehling's solution, but a sample kindly supplied by Dr. Levene depresses the melting point when admixed with it. *l*-Allonolactone recently prepared by Professor W. C. Austin (1), and kindly supplied by him, also proved to be different. Calcd. for $C_6H_{10}O_6$: C, 40.4; H, 5.62%; M.W. 178; calcd. for $C_7H_{12}O_7$: C, 40.39; H, 5.77%; M.W. 208. Found: C, 41.02, 41.01; H, 6.02, 6.02%; M.W. 196, 184 (Rast). The substance does not react with phenylhydrazine. Owing to the small quantity available, a more thorough study will necessarily await the collection of a new lot of material.

Examination of the Resinous Material (B)

The soft, resinous material filtered from the water-insoluble extract was mixed with shredded asbestos with the aid of alcohol which was subsequently evaporated. The hard cake thus formed was ground and extracted in a Soxhlet apparatus successively with petroleum ether, ether, chloroform, ethyl acetate and methanol.

Petroleum Ether Extract

After removal of the solvent by distillation, the residual oil was mixed with the petroleum ether extract of the original material, and the combined oil saponified with alcoholic potassium hydroxide. The cooled basic solution was diluted with an equal volume of water and shaken repeatedly with ether.

Isolation of Myricyl Alcohol, $C_{30}H_{62}O$

The solvent was distilled from the ether extract, the crystalline residue dissolved in boiling acetone and the filtered solution allowed to cool. The crystalline deposit, filtered and washed with cold acetone, was recrystallized several times from hot acetone, and distilled *in vacuo;* it came over at 300° C./2 mm. Recrystallized from ethyl acetate, it melted at 82-83° C. Calcd. for $C_{30}H_{62}O$: C, 82.19; H, 14.18%. Found: C, 82.28, 82.25; H, 14.02, 14.02%. This substance was thus identified as myricyl alcohol.

Isolation of Arisaesterol

After separation of myricyl alcohol, the acetone was evaporated from the mother liquor, and the crystalline residue dissolved in boiling methanol from which the sterol separated as narrow, lustrous plates. Recrystallized several times from hot methanol, the latter melted at 135° C. Calcd. for $C_{36}H_{64}O_2$: C, 81.82; H, 12.12%. Found: C, 81.79; H, 12.17%. This sterol, therefore, belongs to a class of the general formula $C_nH_{2n-8}O_2$. It is proposed to designate it as arisaesterol.

Isolation of Fatty Acids

The fatty acids obtained from the basic solution which has been extracted with ether were separated by the lead-soap–alcohol method into unsaturated and saturated fractions. The unsaturated acids were oxidized with cold, dilute permanganate and the product, by repeated extraction with boiling ethyl acetate, separated into tetrahydroxystearic acid, m.p. 172-173° C., and a small quantity of dihydroxystearic acid, m.p. 126° C. Admixture of the respective acids with authentic specimens caused no depression in melting point. Hence, the unsaturated acids appear to consist of a mixture of linoleic acid with a small amount of oleic acid.

The saturated acids were converted into the methyl esters and fractionated under diminished pressure. The first fraction, 150-156° C./3.5 mm., forming about one-fifth of the total, solidified on cooling to stellate aggregates of stiff, white needles, m.p. 28° C., and consisted of methyl palmitate. At 160-190° C./3.5 mm. a very small amount of a colorless oil distilled over, which, on standing, deposited acicular crystals of methyl palmitate. The residue in the flask was rinsed out with boiling methanol (charcoal) and the clear solution, on cooling, deposited fine, elongated flakes, m.p. 55-56° C. On hydrolysis, the acid was obtained in too small a quantity to permit definite identification.

Ether Extract (Isolation of a Phytosterolin)

The ethereal solution when concentrated to a convenient bulk, deposited a crystalline substance which, when recrystallized from a mixture of pyridine and alcohol, melted at 297° C. Calcd. for $C_{33}H_{56}O_6$: C, 72.25; H, 10.21%. Found: C, 71.76, 71.88; H, 10.49, 10.46%. There is little doubt that this is a phytosterol glucoside belonging to the series $C_nH_{2n-10}O_6$; its behavior in the sterol color reactions, and in Whitby's test for sterolins (8), together with

the failure to cause any depression in melting point when admixed with a specimen of a sterolin obtained from another plant, support this conclusion.

Chloroform, Ethyl Acetate and Methanol Extracts

From the chloroform solution a small quantity of a crystalline substance, m.p. 272° C. (decomp.) was isolated, but this was too minute to permit further work. The ethyl acetate and methanolic solutions yielded gums from which, even after boiling with 10% aqueous sodium hydroxide, nothing crystalline could be obtained.

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

XLVI. STRUCTURE OF THE CELLULOSE SYNTHESIZED BY THE ACTION OF *ACETOBACTER XYLINUS* ON FRUCTOSE AND GLYCEROL[1]

By J. Barsha[2] and Harold Hibbert[3]

Abstract

The membranes synthesized by the action of *Acetobacter xylinus* on fructose and on glycerol have been shown (after suitable purification) by the recognized methods of methylation, acetylation, acetolysis and hydrolysis to be chemically identical with cotton cellulose. These conclusions are confirmed by the results of X-ray analysis.

The X-ray investigation by W. A. Sisson and G. L. Clark indicates the identity of the cellulose membranes formed from glucose, fructose, glycerol, sucrose, galactose and mannitol by the action of *Acetobacter xylinus* and thus lends support to the view that the same polysaccharide is synthesized by the organism whenever cell-wall formation (growth) occurs and that this polysaccharide is chemically identical with cotton cellulose.

Introduction

The formation of cellulose in plants has been studied by relatively few investigators, and it has been generally assumed, in the absence of experimental data, that glucose is the starting material from which cellulose is synthesized.

The knowledge that a simple unicellular organism, *Acetobacter xylinus*, is capable of producing cellulose in the formation and growth of its cell-wall (2, 3) indicated the possibility of using this organism for a study of the substances capable of acting as a starting material for cellulose formation. The fact that the membrane produced during the growth of the bacteria has, after purification, an empirical composition corresponding to $C_6H_{10}O_5$ and gives the so-called "cellulose reaction," namely a violet coloration with zinc chloride and iodine, was regarded by earlier workers (2, 3, 4) as sufficient proof of the cellulosic nature of the membrane. However, Lüdtke (13, 14) has shown that the color reaction is also given by other cell-wall polysaccharides, namely Mannan B and Xylan B. Pringsheim (16, p. 104) believes that the iodine-zinc chloride reaction is not a sufficient differentiation between cellulose and the hemicelluloses. Futhermore, Jordon states, "Among the bacteria, as in the lower fungi generally, cellulose is conspicuous by its absence, but another and somewhat similar carbohydrate, designated as hemicellulose, is often present in abundance" (11, p. 75).

It was therefore necessary, in studying the growth of *Acetobacter xylinus* and the accompanying formation of the cell-wall polysaccharide, to show, in several representative cases, that the polysaccharide of the purified cell-wall substance is actually cellulose.

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The selection of the polysaccharide product obtained during growth of the organism on glucose seemed to be the logical first choice. Complete chemical examination showed this polysaccharide to possess the same chemical structure as cotton cellulose (7). The present investigation relates to the constitution of the cell-wall substance represented by the membrane produced by the action of *Acetobacter xylinus* on fructose and on glycerol. Also in these cases it has been possible to show that the membranes, after suitable purification, have the same empirical composition, *viz.*, $C_6H_{10}O_5$.

Acetylation of the two bacterial celluloses with a mixture of acetic anhydride, glacial acetic acid and sulphuryl chloride as catalyst gave good yields of cellulose triacetates having a specific rotation in chloroform very similar to that of cellulose triacetate prepared from cotton cellulose. Saponification of the triacetates with 2*N* methyl alcoholic sodium hydroxide yielded regenerated celluloses which were shown by analysis to have the same empirical composition as the original bacterial celluloses ($C_6H_{10}O_5$).

Hydrolysis of the cellulose triacetates with methyl alcohol containing 0.9% of hydrogen chloride gave good yields of α- and β-methylglucosides. Direct hydrolysis of the regenerated celluloses (chosen in preference to the original cellulose because of their more finely divided form) with a hydrochloric acid solution of zinc chloride was followed polarimetrically and it was found that the end specific rotation approximated very closely to that of pure glucose in the same solvent.

Further proof of the chemical identity of the two bacterial celluloses was found in the experimental proof of the same type of linkage (1, 4) between the glucose units. Trimethyl celluloses were prepared by deacetylation and methylation of acetone-soluble cellulose acetates, followed by further methylations. The respective trimethyl celluloses yielded, on hydrolysis, 2,3,6-trimethyl methylglucoside which was hydrolyzed further to 2,3,6-trimethyl glucose. Additional confirmation was obtained in the preparation of cellobiose octacetate by direct acetolysis of the bacterial celluloses with acetic anhydride and concentrated sulphuric acid.

Unlike the quantitative conversion of starch to maltose, the decomposition of cellulose to cellobiose octacetate has never resulted in high yields, owing presumably to the further decomposition of this latter substance to glucose pentacetate. The best yields reported in the literature, *e.g.* Spencer (18), 45%, were obtained during extensive investigations on the determination of the optimum conditions for acetolysis of cotton cellulose.

It was not deemed advisable in the present investigation to determine the optimum conditions for cellobiose octacetate formation from the bacterial celluloses because of the length of time required.

In an investigation of the α-celluloses from five different kinds of wood, Bell (1) found that these substances apparently contained a cellulose fraction more resistant to complete methylation so that the maximum methoxyl content attained was only 36.3–39.1%. Direct methylation of bacterial cellulose (prepared from glucose) with dimethyl sulphate and 30% sodium

hydroxide yielded a product with a methoxyl content of 43.9%, indicating the absence in the bacterial cellulose of a similar "resistant portion" such as was found by Bell in the wood α-celluloses.

On the basis of the experimental results obtained in this and other investigations (7) it would seem that the same polysaccharide is synthesized by *Acetobacter xylinus* whenever cell-wall formation (growth) occurs and that this polysaccharide is chemically identical with cotton cellulose.

Further support is given to the above conclusion in the results of X-ray examination of a number of bacterial celluloses prepared in this laboratory. The X-ray work was carried out by Dr. W. A. Sisson in collaboration with Dr. George L. Clark, Department of Chemistry, University of Illinois. They found (17) the purified bacterial membranes to be composed of well developed crystallites of cellulose which have a preferential orientation with respect to the surface of the sheet, similar to that reported by Mark and Susich (15) for stretched tunicin and "biosynthetic cellulose." In the case of the membranes prepared from mannitol and galactose, the specimens of the wet and highly swollen membranes were dried under a greater tension than the other samples, with the result that they show a greater degree of preferred orientation (as shown by the intensity being greater over certain sections of the X-ray diffraction rings).

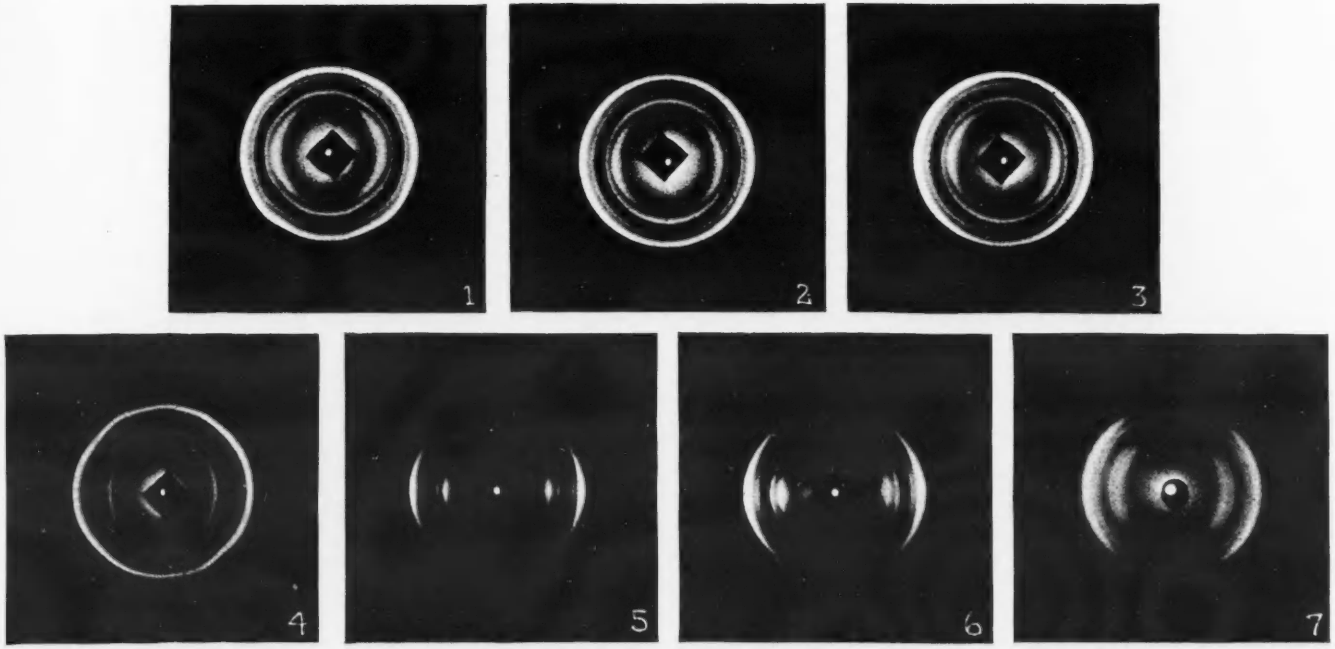
The synthesis of the same polysaccharide, cellulose, by *Acetobacter xylinus* from glucose, fructose, glycerol, sucrose, mannitol and galactose, would indicate the ability of the organism to carry out the many transformations required to convert all of these substances into the common product which serves as the starting material for cellulose formation. It has been generally assumed (5, 12, 19), in the absence of positive experimental proof, that this starting material is glucose.

A comparison of the compounds prepared from cotton and bacterial celluloses is given in Table I.

Experimental

Preparation, Purification and Analysis of Bacterial Celluloses from Fructose and Glycerol

The detailed procedure for the preparation from fructose and glycerol of the bacterial celluloses used in this investigation has been described by Tarr and Hibbert (20). In brief, a solution containing 5–10% of the carbon compound (fructose or glycerol), 1% potassium dihydrogen phosphate, 0.2% sodium chloride and 0.2% asparagine was inoculated with *Acetobacter xylinus* and incubated for about two weeks at 30° C. Examination under the microscope of the highly swollen membrane which formed on the surface of the liquid in the culture vessel revealed, after staining, a conglomeration of rod-like bacterial cells. It is to be noted that in the preparation of the membranes, a nutrient medium was used which did not support growth in the absence of the carbon compound.



X-ray diagrams of cotton and bacterial celluloses. FIGS. 1-6. *Bacterial cellulose from: 1, glucose; 2, fructose; 3, glycerol; 4, sucrose; 5, galactose; 6, mannitol.* FIG. 7. *Cotton fibre.*

PLATE I

TABLE I

COMPARISON OF COMPOUNDS PREPARED FROM COTTON AND BACTERIAL CELLULOSES

Starting material	Cellulose triacetate		α- and β-methyl glucosides from cellulose triacetate		Trimethyl cellulose			
	*$[\alpha]_D$ in $CHCl_3$	Yield, %	Equil. rotation in CH_3OH–HCl	Yield, %	$[\alpha]_D$ in $CHCl_3$	M.p.,† °C.	OCH_3, %	Yield, %
Cotton cellulose (6, 9, 10, 18)	−22.3°	99.5	+106–108°	95.5	−10°	215–216	45.6	85–98
Bacterial cellulose from:								
glucose (7)	−21.9°	98.8	+107.5°	94.1	− 9.2°	231–232	44.0	84.6
fructose	−21.0°	94.5	+105.9°	92.5	− 7.9°	227–230	44.1	82.6
glycerol	−21.8°	97.9	+105.3°	92.2	− 8.8°	232–234	44.4	79.4

Starting material	2,3,6-Trimethyl methylglucoside				2,3,6-Trimethyl glucose			Cellobiose octacetate		
	$[\alpha]_D$ in $CHCl_3$	B.p., °C.	Refractive index	Yield (crude), %	$[\alpha]_D$ in CH_3OH	M.p., °C.	Yield, %	$[\alpha]_D$ in $CHCl_3$	M.p., °C.	Yield, %
Cotton cellulose (6, 9, 10, 18)	+66.0°	115–118 (0.5 mm.)	1.4590	95	+66.5°	104–108	86	41–41.8°	227.5–228	45
Bacterial cellulose from:										
glucose (7)	+64.4°	111.5–115 (0.35–0.40 mm.)	1.4560 (25° C.)	92.3	+65.2°	105–108	83.5	41.0°	222–223	27.3
fructose	+66.7°	110–113 (0.25–0.30 mm.)	1.4555 (25° C.)	96.0	+66.2°	104–106	96.8	40.8°	222–223	29.0
glycerol	+68.5°	109–113 (0.25 mm.)	1.4553 (25° C.)	99.0	+67.7°	102–104	87.0	40.4°	223.5–224	22.9

*For temperatures see Experimental Part.
†The difference in melting point is due to the incompleteness of the methylation.

The membranes were washed with repeated changes of distilled water to remove the water-soluble materials, including the sugars, until the wash waters no longer reduced Fehling's solution. They were then immersed in 2% sodium hydroxide solution, placed in an autoclave (100° C.) for 30 min. and then washed with distilled water until neutral to phenolphthalein. To remove last traces of alkali they were immersed in cold 1% acetic acid and finally washed with large volumes of distilled water. Microscopic examination of the moist membrane after washing showed that the bacterial cells had been disintegrated since no structural forms were visible.

The yield of the pure dried membrane was relatively low, *i.e.*, 2–5% of the weight of the carbon compound used as substrate. The cellulose so obtained from fructose and from glycerol* is completely insoluble in all ordinary organic solvents. The usual fusion test with potassium showed the absence of nitrogen. The combustion analyses were carried out on samples which had been dried at 100° C./1 mm. over phosphorus pentoxide. Analysis:—*A*, Found: C, 44.81, 44.20; H, 6.38, 6.36%. Calcd. for $C_6H_{10}O_5$: C, 44.42; H, 6.20%. *B*, Found: C, 44.58, 44.32; H, 6.31, 6.36%.

Preparation of Cellulose Triacetate

This was carried out according to the modification of Barnett's method devised by Irvine and Hirst (9). One part of bacterial cellulose was acetylated at 65–70° C. with 7.5 parts of glacial acetic acid and 17.5 parts of acetic anhydride with nascent sulphuryl chloride as catalyst. The acetylation mixture was diluted with two volumes of acetone, dropped into five volumes of distilled water at 90° C. whilst stirring rapidly, and the precipitate filtered and washed thoroughly with distilled water until free from acid.

Bacterial cellulose *A* (10 gm.; moisture, 6.51%) yielded 15.70 gm. of cellulose triacetate (94.5%). In chloroform, $[\alpha]_D^{25} = -21.0°$ (c = 1.666). Analysis:—Found: CH_3CO, 44.7%. Calcd. for $C_6H_7O_5(CH_3CO)_3$: CH_3CO, 44.8%.

Cellulose *B* (9.47 gm.; moisture, 6.22%) yielded 15.45 gm. of cellulose triacetate (97.9%). In chloroform, $[\alpha]_D^{27} = -21.8°$ (c = 1.231). Analysis:–Found: CH_3CO, 44.2%.

Regeneration of Cellulose from the Cellulose Triacetates A and B

Two grams of each cellulose triacetate was saponified by immersing in 50 cc. of 2*N* methyl alcoholic sodium hydroxide solution at room temperature for 24 hr. The regenerated cellulose was filtered and washed thoroughly until free from alkali.

Cellulose triacetate *A* (2.00 gm.) yielded 1.10 gm. of regenerated cellulose (97.8%). Analysis:—Found: C, 43.98; H, 6.23%. Calcd. for $C_6H_{10}O_5$: C, 44.42; H, 6.20%.

Cellulose triacetate *B* (2.00 gm.) yielded 1.03 gm. of regenerated cellulose (91.6%). Analysis:—Found: C, 44.23; H, 6.39%.

*Throughout the experimental part of this paper preparations derived from the bacterial cellulose prepared from fructose will be designated by *A* whilst those derived from the bacterial cellulose prepared from glycerol will be designated by *B*.

Hydrolysis of the Cellulose Triacetates A and B to α- and β-Methylglucosides

About four grams of each cellulose triacetate was hydrolyzed with 60 cc. of dry methyl alcohol containing 0.9% hydrogen chloride in a sealed bomb-tube at 125° C. for 60 hr. The acid was then neutralized with silver carbonate, the solution filtered and the filtrate decolorized with charcoal. The alcohol was evaporated under diminished pressure in a tared flask. The semi-crystalline product was redissolved in hot ethyl alcohol which was then evaporated at 60° C./10 mm. A crystalline product was obtained.

Dry cellulose triacetate *A* (3.82 gm.) yielded 2.37 gm. of α- and β-methyl-glucosides (92.5%). In a solution of methyl alcohol containing 0.9% hydrogen chloride, the mixed glucosides showed $[\alpha]_D^{26} = +97.8°$ (c = 0.9924). After heating in a sealed tube at 100° C. for six hours a portion of this same solution had a constant specific rotation of +105.9°. Fractional crystallization of the mixed glucosides from absolute ethyl alcohol yielded the characteristic crystals of α-methylglucoside melting at 163.5° C. In water, $[\alpha]_D^{26} = +156.6°$ (c = 0.920). The mother liquor from the recrystallization, which contained an excess of β-methylglucoside, was evaporated to dryness under diminished pressure and the residue was dissolved in methyl alcohol containing 0.9% hydrogen chloride. This solution was heated for 15 hr. in a sealed tube at 100° C. to re-establish the equilibrium. A portion of this solution showed $[\alpha]_D^{26} = +106.3°$ (c = 1.016).

Dry cellulose triacetate *B* (3.96 gm.) yielded 2.46 gm. of α- and β-methyl-glucosides (92.2%). A solution of the mixed glucosides in methyl alcohol (0.9% hydrogen chloride) showed $[\alpha]_D^{26} = +96.5°$ (c = 1.026) which increased on heating as above to a constant specific rotation of +105.3°. Fractional crystallization yielded α-methylglucoside; m.p. 165° C. In water, $[\alpha]_D^{25} = +156.7°$ (c = 0.5934). Re-establishment of the equilibrium was brought about by heating as before. In methyl alcohol (0.9% hydrogen chloride), $[\alpha]_D^{26} = +105.2°$ (c = 1.112).

Hydrolysis of Cellulose A and Cellulose B with Zinc Chloride-Hydrochloric Acid

The method employed was that of Hibbert and Percival (8) in which the course of the hydrolysis of cellulose dissolved in zinc chloride-hydrochloric acid is followed by observing the change in rotation of the solution. The procedure has been described in detail elsewhere (7, p. 587). In the same solvent, pure anhydrous glucose showed $[\alpha]_D^{23} = +67.5°$ (c = 1.0028).

Regenerated cellulose *A* (0.5049 gm.) was dissolved in 50 cc. of solvent (c = 1.0098). The observed specific rotations are given in Table II and plotted in Fig. 8.

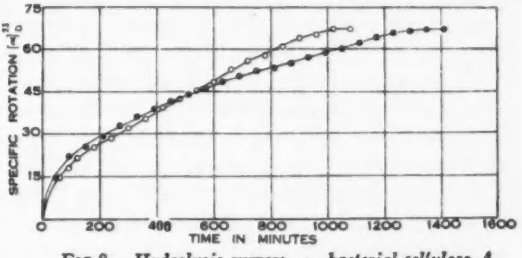


FIG 8. *Hydrolysis curves:* •, *bacterial cellulose A (from fructose);* ○, *bacterial cellulose B (from glycerol).*

TABLE II

HYDROLYSIS OF BACTERIAL CELLULOSE *A* IN ZINC CHLORIDE–HYDROCHLORIC ACID SOLUTION

Time, min.	$[\alpha]_D^{25}$	Time, min.	$[\alpha]_D^{25}$	Time, min.	$[\alpha]_D^{25}$	Time, min.	$[\alpha]_D^{25}$
0	0	390	38.8	810	53.3	1230	65.7
45	+14.6°	450	41.6	870	55.0	1290	66.3
90	22.0	510	44.0	930	57.0	1350	66.8
150	25.5	570	46.2	990	58.4	1410	+66.8
210	29.1	630	48.4	1050	60.1		
270	32.8	690	50.4	1110	62.0		
330	36.0	750	52.2	1170	64.0		

Regenerated cellulose *B* (0.2536 gm.) was dissolved in 50 cc. of solvent (c = 0.5072). The observed specific rotations are given in Table III and plotted in Fig. 8.

TABLE III

HYDROLYSIS OF BACTERIAL CELLULOSE *B* IN ZINC CHLORIDE–HYDROCHLORIC ACID SOLUTION

Time, min.	$[\alpha]_D^{25}$	Time, min.	$[\alpha]_D^{25}$	Time, min.	$[\alpha]_D^{25}$	Time, min.	$[\alpha]_D^{25}$
0	0	240	28.3	540	45.5	840	60.9
60	+14.8°	300	32.0	600	48.6	900	64.0
90	17.9	360	35.1	660	52.9	960	65.2
120	21.5	420	39.4	720	56.0	1020	67.1
180	25.2	480	42.5	780	57.8	1080	+67.1

Preparation of Trimethyl Cellulose by Deacetylation and Methylation of Cellulose Acetates A and B

Cellulose acetate *A* (10.00 gm.; CH_3CO, 42.3%) was dissolved in 300 cc. acetone and simultaneous deacetylation and methylation effected with 320 cc. of sodium hydroxide solution (30% by weight) and 120 cc. of dimethyl sulphate. The reagents were added in 10 portions, one every 15 min. at 56° C. At the end of the reaction, the acetone was distilled off, the mixture heated to 95° C., filtered immediately through a steam jacketed Büchner funnel and washed thoroughly with boiling distilled water. Analysis:—Found: CH_3O, 38.13%. Calcd. for trimethyl cellulose: CH_3O, 45.6%.

The product was dissolved in 125 cc. of pyridine and reacetylated with 70 cc. of acetic anhydride at 50° C. for five days. The solvents were removed at 40–50° C./10 mm. The residue was taken up in 500 cc. of benzene and precipitated by dropping into 1250 cc. of cold petroleum ether (b.p. 30–50° C.) with rapid stirring. It was centrifuged and washed with more petroleum ether. This material was then suspended in 150 cc. of acetone and methylated as before. Analysis:—Found: CH_3O, 42.74%. The product was subjected to reacetylation and a third methylation. Analysis:—Found: CH_3O, 43.33%.

A final methylation was then performed with Purdie's reagents as described previously (7, p. 589). Yield from cellulose acetate *A*; 6.00 gm. (82.6%

of theory for trimethyl cellulose). Analysis:—Found: C, 52.86, 52.27; H, 7.88, 7.77; CH_3O, 44.1%. Calcd. for $C_6H_7O_5(CH_3)_3$: C, 52.91; H, 7.90; CH_3O, 45.6%. The trimethyl cellulose *A* showed in chloroform, $[\alpha]_D^{26} = -7.9°$ (c = 1.262); in benzene $[\alpha]_D^{26} = -14.2°$ (c = 1.057). M.p., 227–230° C.

Cellulose acetate *B* (12.00 gm.; CH_3CO, 41.0%) was dissolved in 240 cc. of acetone and methylated in the same manner with 385 cc. of 30% sodium hydroxide solution and 145 cc. of dimethyl sulphate. Yield, 8.32 gm. (93.4%). Analysis:—Found: CH_3O, 41.7%.

A portion (4.0 gm.) of the product was dissolved in 40 cc. of pyridine and acetylated with 10 cc. of acetic anhydride for 48 hr. at room temperature. The product, obtained as before, was suspended in 100 cc. of acetone and methylated in the usual way. Analysis:—Found: CH_3O, 44.0%. A second reacetylation and methylation produced no increase in the methoxyl content.

Part of the methylated product (3.5 gm.) was dissolved in 110 gm. of methyl iodide and treated as before with 40 gm. of dry silver oxide. Yield, 3.4 gm. (79.4%). Analysis:—Found: C, 53.05, 52.65; H, 8.10, 8.00; CH_3O, 44.4%. Trimethyl cellulose *B* showed, in chloroform, $[\alpha]_D^{25} = -8.8°$ (c = 1.130); in benzene, $[\alpha]_D^{26} = -15.2°$ (c = 1.055). M.p., 232–234° C.

Direct Methylation of Bacterial Cellulose (from Glucose)

Dry bacterial cellulose (5.13 gm., prepared by the action of *Acetobacter xylinus* on glucose) was suspended in 350 cc. of acetone and methylated with 200 cc. of dimethyl sulphate and 460 cc. of sodium hydroxide solution (30%) at 56° C. The product was worked up in the usual manner. Eight such methylations in all were carried out. Yield, 5.20 gm. (80.5%). Analysis:—Found: CH_3O, 43.93%.

Hydrolysis of Trimethyl Celluloses A and B to 2,3,6-Trimethyl Methylglucosides

Well dried trimethyl cellulose *A* (2.70 gm.; CH_3O, 44.1%) and 40 cc. of pure methyl alcohol containing 1% of hydrogen chloride were heated in a bomb tube at 100° C. for 50 hr. as already described (7, p. 589). Yield, 3.00 gm. (96% of theory, calculated for conversion of trimethyl cellulose to trimethyl methylglucoside).

The product was dissolved in dry ether and transferred to a 5-cc. Claissen flask in which the ether was evaporated off. The trimethyl methylglucoside was then distilled under diminished pressure. A colorless, viscous liquid (2.64 gm.) was obtained; b.p., 110–113° C./0.25–0.30 mm. Refractive index = 1.4555 (25° C.). In chloroform, $[\alpha]_D^{24} = +66.9°$ (c = 1.151). Analysis:—Found: CH_3O, 52.3%. Calcd. for $C_6H_8O_6(CH_3)_4$: CH_3O, 52.6%.

Trimethyl cellulose *B* (2.13 gm.; CH_3O, 44.4%) and 35 cc. of pure methyl alcohol containing 1% of hydrogen chloride were heated in a bomb tube at 100° C. for 50 hr. The product was isolated as before. Yield, 2.44 gm. (99.0%). Distillation yielded 2.13 gm. of a colorless, viscous liquid. B.p., 109–113° C./0.25 mm. Refractive index, 1.4552 (25° C.). In chloroform, $[\alpha]_D^{26} = +68.5°$ (c = 1.358). Analysis:—Found: CH_3O, 51.1%.

Preparation of 2,3,6-Trimethyl Glucose from Trimethyl Celluloses A and B

Trimethyl methylglucoside *A* (2.02 gm.) dissolved in 125 cc. of 5% hydrochloric acid was heated under reflux for 10 hr. in the manner described (7, p. 590). A sirup was obtained which crystallized on cooling. Yield, 1.84 gm. (96.8%). After one recrystallization from dry ether, the needle-like crystals melted at 104–106° C. In methyl alcohol, containing a trace of hydrogen chloride, the product showed $[\alpha]_D^{26} = +66.2°$ (c = 0.5287).

Trimethyl methylglucoside *B* (1.65 gm.) was hydrolyzed under reflux with 100 cc. of 5% hydrochloric acid solution for 12 hr. The product was worked up as before. Yield, 1.35 gm. (87%). One recrystallization from dry ether yielded crystals melting at 102–104° C. In methyl alcohol containing a trace of hydrogen chloride, $[\alpha]_D^{25} = +67.7°$ constant (c = 0.992).

Acetolysis—Preparation of Cellobiose Octacetates A and B

Dry bacterial cellulose *A* (2.03 gm.) was subjected to acetolysis by treatment with 8 cc. of acetic anhydride and 0.2 cc. of concentrated sulphuric acid for 19 days at 50° C. The reaction mixture was then diluted with 10 cc. of glacial acetic acid, well stirred, and dropped into 500 cc. of cold distilled water. After standing overnight at room temperature, the precipitate was filtered and washed with distilled water until free from acid. The air dried precipitate was then extracted under reflux with three 100-cc. portions of 95% alcohol and filtered hot. The combined extracts were decolorized with charcoal and filtered hot. The crystals of cellobiose octacetate which separated out on cooling were filtered on to a tared Gooch crucible. The mother liquor was evaporated to 50 cc. and cooled. A further amount of cellobiose octacetate was obtained. Yield, 1.23 gm. (29%). After two recrystallizations from ethyl alcohol, the cellobiose octacetate showed, in chloroform, $[\alpha]_D^{24} = +40.8°$ (c = 1.777) and melted at 222–223° C.

Bacterial cellulose *B* (2.10 gm.) was subjected to acetolysis as above. Yield, 1.05 gm. (22.9%). (A small amount of product was accidentally lost during extraction.) After two recrystallizations from ethyl alcohol, the cellobiose octacetate showed, in chloroform, $[\alpha]_D^{23} = +40.4°$ (c = 0.790). M.p., 223.5–224° C.

Bacterial cellulose (1.96 gm., prepared from glucose) was subjected to acetolysis. Yield, 1.12 gm. of cellobiose octacetate (27.3%). The product was recrystallized twice from ethyl alcohol. In chloroform, $[\alpha]_D^{22} = +41.0°$ (c = 0.712). M.p., 222–223° C.

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THE INFLUENCE OF TEMPERATURE ON THE RATE OF NATURAL PENETRATION OF ELECTROLYTES INTO WOOD[1]

By O. Maass[2]

Abstract

The rates of diffusion of sodium hydroxide, sodium chloride and hydrochloric acid into chips of black spruce heartwood impregnated with water were measured for different shapes of chip at 20, 50, and 75° C. In the longitudinal direction of the wood, hydrochloric acid diffuses the most rapidly and sodium hydroxide and sodium chloride at nearly the same rates. In the lateral direction sodium hydroxide diffuses the most rapidly, owing to its action on the wood. Concentration of electrolyte is practically without influence on the time to half-value for sodium hydroxide and hydrochloric acid. The density of the wood does not affect the rate of diffusion of sodium hydroxide.

The rate of diffusion of water into air dry chips was measured at 20 and 50° C.

Introduction

In order to understand the mechanism of the cooking of wood with alkalies, it is necessary to understand related phenomena. Among these are included: *(a)* the sorption of sodium hydroxide on wood; *(b)* the manner in which liquids penetrate into wood containing air, and the influence of various factors on the rate at which impregnation of the wood takes place; *(c)* the natural penetration, or diffusion, of the cooking reagent into chips during the cooking process when the chips are completely impregnated with liquor.

Data relating to these three problems were obtained by Richardson and Maass (2), who carried out experiments at room temperatures. The present work was begun as an investigation of the influence of temperature on the rate of diffusion of electrolytes into wood, with a view to ascertaining the relation of data to actual cooking conditions. At the same time some experiments were made on the rate of natural penetration of water into air dry wood. Experiments have also been carried out in an attempt to explain the differences in the rates of diffusion of sodium hydroxide, sodium chloride and hydrochloric acid into wood chips impregnated with water.

For comparison of results, the general details of experimental procedure as devised by Richardson and Maass (2) were followed in the present work; *i.e.*, chips of black spruce heartwood, of square cross section and weight 2.75 gm. (oven dry) were used. The concentration of the electrolytes was 1.27 molar except in the experiments on the effect of concentration. A modified form of diffusion cell, however, was used.

Fig. 1 shows a side-view of the diffusion cell, containing a chip surrounded by solution. *B* is a section of the conductivity cell by means of which the resistance of the solution was measured. The inner tube (2) was used with chips of length greater than 2.5 cm. The chief purpose of this inner tube was

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to minimize the amount of solution necessary to cover the chip completely, so that the concentration change would be as large as possible, with a resulting accuracy in measurement. The solution was drawn up into the inner tube and the level maintained by a clamp on a rubber tube attached to the inner tube at (4). When making a measurement this clamp was released, allowing the solution to run down into the main body of the cell where it was thoroughly stirred by alternately sucking up and blowing solution out of the electrode chambers and the inner tube. The temperature of the solution was kept constant throughout an experiment by placing the cell in a water bath equipped with an automatic temperature regulator and a constant level syphon to compensate for evaporation from the bath at the higher temperatures.

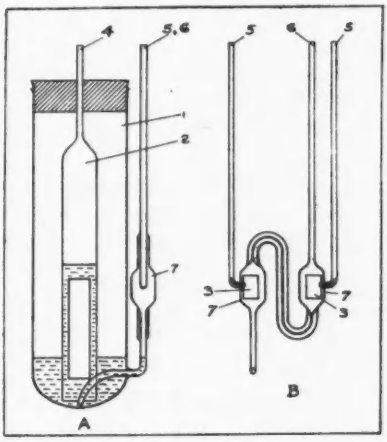

FIG. 1. *Diffusion cell.*

When a chip, impregnated with water, is placed in a solution of an electrolyte, the concentration changes as electrolyte diffuses into the chip. This change in concentration provides a means of measuring the rate of diffusion. Knowing the original concentration, the weight of solution and the weight of water in the chip, the final concentration can be calculated. The concentration corresponding to the diffusion of one-half of the electrolyte finally diffusing into the chip can then be calculated, which makes it unnecessary to continue an experiment much after the half-value has been reached. This procedure eliminates to a large extent errors caused by loss of water vapor from the cell at higher temperatures while waiting for the concentration to reach equilibrium.

The final and one-half values of the concentrations were changed to the corresponding resistance values, assuming the change in resistance to be proportional to the change in concentration, since the observed change in concentration was small. The relation between the changes in resistance and concentration was obtained in a control experiment, in which wood in the form of thin sections at right angles to the grain ("wood flake") was used instead of a chip. In such an experiment the diffusion was very rapid and the solution reached equilibrium before such errors as loss of water vapor became appreciable.

In the experiments with sodium hydroxide, the change in concentration was followed by titrating weighed samples of solution after known intervals of time, since it was found that the resistance did not reach a constant value. Besides the change in concentration due to the diffusion of electrolyte into the chip, there is a further change, amounting to about 25% of the total

change, due to sorption of alkali by the wood. The sorption value is known from experiment and its effect on the final concentration can be calculated. (In the cases of sodium chloride and hydrochloric acid sorption is negligible.)

One effect of sorption is to increase the amount of alkali which has to diffuse into a chip before the half-value is reached. At the same time, however, sorption increases the concentration gradient, which in turn would be expected to increase the rate of diffusion and so tend to offset the effect of the larger amount of alkali. Inasmuch as it is impossible to measure or to estimate the extent of these two effects, they have been neglected as far as the calculations are concerned. Because of sorption, the comparison of the rates of diffusion of sodium hydroxide with the values for sodium chloride and hydrochloric acid is not strictly valid. The measured rate of diffusion of sodium hydroxide is probably less than the true value, which would be obtained if sorption were absent.

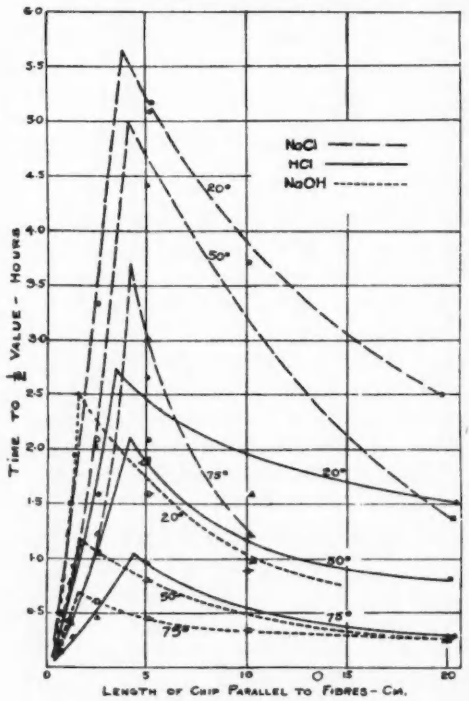

FIG. 2. *Diffusion of sodium chloride, sodium hydroxide, and hydrochloric acid into black spruce chips impregnated with water.*

Concentration in the case of sodium hydroxide, or resistance in the case of sodium chloride and hydrochloric acid, was plotted against time, and from the curve the time to half-value, or half-diffusion, was obtained. This quantity was used as a basis for comparison of rates of diffusion.

A consideration of the errors in measurement, and especially errors introduced by the use of temperatures as high as 75° C., showed that the accuracy obtained in these experiments was greater than that necessary, taking into account the variable nature of the wood.

Results and Discussion

Of those factors which influence the rate of diffusion the following have been investigated: (i) chip length, (ii) temperature change, (iii) concentration of electrolyte, and (iv) wood density.

Effect of (i) Chip Length, and (ii) Temperature Change

In Table I are given the data obtained for the three electrolytes at different temperatures and for different chip lengths. These values are plotted in Fig. 2.

TABLE I

EFFECT OF CHIP LENGTH AND TEMPERATE CHANGE

Sodium hydroxide		Hydrochloric acid		Sodium chloride	
Chip length, cm.	Time to half-diffusion, $T_{½}$, min.	Chip length, cm.	Time to half-diffusion, $T_{½}$, min.	Chip length, cm.	Time to half-diffusion, $T_{½}$, min.
At 20° C.					
.66	30	.17	3.0	.64	30
1.32	90	.66	19	1.30	116
2.59	125	1.22	47	2.57	200
4.88	113	2.57	95	5.24	310
5.13	95	5.10	125	5.16	305
10.3	53	5.08	158	19.8	150
		20.4	91		
At 50° C.					
.32	9.0	.18	2.0	.18	2.0
.69	23.0	.30	5.0	.38	6.5
1.29	46	.69	7.0	.69	16.0
2.54	63	1.22	25	1.30	55
5.16	47	2.54	93	2.36	121
10.3	20	5.03	115	5.03	264
20.0	16	10.1	73	10.08	222
		20.1	49	20.3	82
At 75° C.					
.64	13.0	.32	3.0	.32	6.0
1.22	25.0	1.30	16.0	1.27	25.0
2.59	36.0	2.54	27.5	2.54	73
5.11	26.0	5.08	57.0	5.08	180
10.4	20.0	20.3	17.0	10.2	58
20.3	16.0			10.1	95

It is seen that each curve gives a maximum value which corresponds to the length of chip into which the electrolyte concerned diffuses at a minimum rate. The other dimensions of this chip when calculated indicate the "worst shape" of chip. The manner in which this shape varies for the three electrolytes is illustrated in Fig. 3. The experimental accuracy, which is limited chiefly by the wood, does not appear to be such that a distinction may be made between the worst shapes of chip for sodium chloride and hydrochloric acid diffusions.

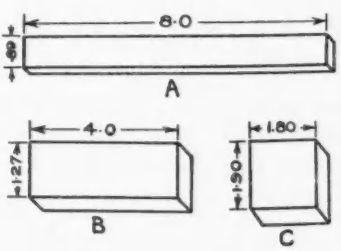

FIG. 3. *"Worst shape" of chips for diffusion of sodium hydroxide, sodium chloride, hydrochloric acid and water into black spruce. A, Water into air dry wood at 50° C.; B, sodium chloride and hydrochloric acid; C, sodium hydroxide.*

The rates of diffusion of electrolytes into chips of the worst shape decrease rapidly in the order sodium hydroxide, hydrochloric acid and sodium chloride (Fig. 4). Over the temperature range studied, the rate of diffusion increases in proportion to the temperature rise. The worst shape of chip for diffusion of sodium hydroxide is practically a cube, which means that the rate of diffusion per unit area of the side of a chip is about one-half that for the end of a chip. Under cooking conditions the alkali would be expected to open up the wood structure, so that diffusion in such a case is probably equally rapid into both side and end of a chip.

Furthermore, the rate of diffusion of sodium hydroxide into a chip in the form of a cube of about 1.8 cm. (0.7 in.) side increases about four times when the temperature is raised from 20 to 75° C. The indication then is that at cooking temperatures the rate of diffusion is so rapid into a chip of the much smaller size used in commercial practice that the concentration of alkali is practically constant in all parts of the chip being cooked. Chip shape appears to be of minor importance as far as the cooking operation is concerned, but inasmuch as the chips used commercially contain air, which is an almost unknown factor influencing the initial diffusion of liquor into the chips, the shape of chip should be such as to permit the most rapid impregnation of the chip with liquor.

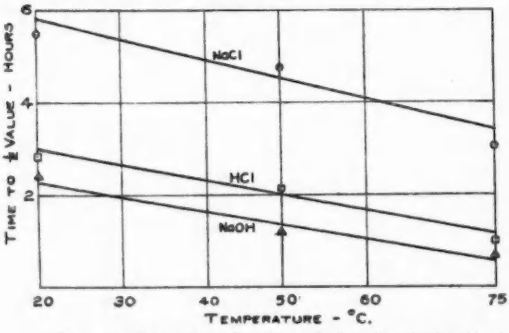

FIG. 4. *Diffusion of sodium hydroxide, hydrochloric acid and sodium chloride into chips of the "worst shape".*

(iii) Effect of Concentration of Electrolyte

Chips of length 0.64 cm. were used in these experiments, the results of which are given in Table II. It was concluded that concentrations above

TABLE II

EFFECT OF CONCENTRATION OF SODIUM HYDROXIDE

Molar conc. of NaOH	.24	.30	.50	1.06	2.9	6.6	13.5	13.5
$T_{½}$, min.	33.0	34.0	25.0	17.0	15.0	17.5	12.0	17.0

1.06 molar have no effect on the time to half-value for sodium hydroxide. Similar results were obtained with hydrochloric acid of concentrations between 0.38 and 1.37 molar (Table III). No experiments were made on the effect of concentration on the rate of diffusion of sodium chloride.

TABLE III

EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID

Chip length, cm.	$T_{½}$, min.		Chip length, cm.	$T_{½}$, min.	
	0.38 *M* HCl	1.37 *M* HCl		0.38 *M* HCl	1.37 *M* HCl
0.64	7.0	8.0	1.27	25.0	21.0

(iv) Effect of Density of Wood

The wood used in these experiments was very close grained, having 40-60 annual rings per inch and a density of 0.55. The results are given in Table IV in comparison with values for wood having 15-20 rings per inch and a density of 0.40, and it is seen that the same time to half-value obtains in the case of both close grained and open grained wood. Wood density therefore does not influence the rate of diffusion of sodium hydroxide into a chip.

TABLE IV

EFFECT OF DENSITY OF WOOD ON RATE OF DIFFUSION OF SODIUM HYDROXIDE AT 20° C.

Chip length, cm.	$T_{½}$, min.		Chip length, cm.	$T_{½}$, min.	
	Close grained wood	Open grained wood		Close grained wood	Open grained wood
0.61	37	30	2.69	125	125
1.37	75	90	5.33	120	113

(v) Effect of Wood Structure

Information regarding the rates of diffusion of the three electrolytes in the two main directions of the wood structure may be obtained from a further study of the curves in Fig. 2. Theoretical considerations are also of interest in this connection, for the diffusion process is in a sense an ionic one, and, since hydrogen ions diffuse very rapidly, hydrochloric acid would be expected to diffuse the most rapidly of the three electrolytes studied, and sodium hydroxide and sodium chloride at nearly the same rates.

In a very short chip, most of the diffusion takes place through the ends of the chip, but in a very long chip most of the diffusion takes place through the sides. In the portion of an isotherm (Fig. 2) to the left of the maximum, then, longitudinal diffusion is the predominating effect, but for the right part of the curve lateral diffusion predominates. The left parts of the isotherms indicate that for longitudinal diffusion, hydrochloric acid diffuses the most rapidly, and sodium hydroxide and sodium chloride at nearly the same rates, as would be expected for reasons mentioned above. The right parts of the isotherms, however, indicate that while the expected order of the relative

rates of diffusion obtains in the cases of sodium chloride and hydrochloric acid, sodium hydroxide diffuses much more rapidly in the lateral direction of the wood structure than either of the other two electrolytes.

More data relating to the diffusion of sodium hydroxide and sodium chloride have been obtained in the following series of experiments in which were investigated: (1) the effect of pretreating a chip with sodium hydroxide, on the rate of diffusion of sodium chloride, (2) the rates of diffusion of sodium hydroxide and sodium chloride into chips whose sides were coated with wax so that diffusion could take place only in the longitudinal direction, and (3) the effect of concentration of the sodium hydroxide, used in pretreating the wood, on the rate of diffusion of sodium chloride. All these experiments were carried out at room temperature.

TABLE V

EFFECT OF PRETREATMENT WITH SODIUM HYDROXIDE ON RATE OF DIFFUSION OF SODIUM CHLORIDE INTO A CHIP (20° C.)

NaCl into untreated chip	NaCl into penetrated chip	NaOH into untreated chip
$T_{1/2}$ min.		
310	100	113
305	140	95

Sodium hydroxide was allowed to diffuse into a chip until sorption equilibrium was reached. The chip was then washed in water until all the alkali had diffused out. The rate of diffusion of sodium chloride into the pretreated chip was found to be almost as great as that of sodium hydroxide, as shown by the data in Table V, which were obtained in experiments on 5.1-cm. chips.

In order to find out whether the action of the alkali increases the longitudinal or the lateral diffusion of the sodium chloride, or both, a series of experiments was carried out on two 5.0-cm. presoaked chips whose sides were coated with wax. The rate of diffusion of sodium chloride was measured for each chip, which was then placed in water until all the sodium chloride had diffused out. The rate of diffusion of sodium chloride into the chip was measured again as check on the previous measurement and to see what accuracy might be expected in these experiments. Three more diffusion measurements were then made on each chip. The order in which the electrolytes were used was sodium hydroxide, sodium chloride and sodium hydroxide. One to two weeks was necessary between diffusion measurements in order to allow the electrolyte to diffuse completely out of the wood before another experiment could be made. The results of these experiments are given in Table VI.

In the first experiments with sodium chloride and sodium hydroxide, the latter appears to have diffused somewhat faster than the former, but experimental accuracy is not such that a definite conclusion may be drawn. The last diffusion experiments indicate that the previous treatment of the wood with sodium hydroxide decreased the rate of longitudinal diffusion for both electrolytes. This result may mean that there occurred swelling of the

membranes at the bordered pits, or of the walls of the tracheids, which reduced the effective diameter of the fibre cavities.

These experiments show that there is little difference in the rates of diffusion of sodium hydroxide and sodium chloride in the fibre direction of the wood. Since the rate of diffusion of sodium chloride into a chip of the shape used in these experiments is much less than that of sodium hydroxide, the lateral diffusion of sodium hydroxide must be much greater than that of sodium chloride, thus confirming a previous conclusion based on the curves of Fig. 2. The more rapid lateral diffusion of sodium hydroxide may be due to: (i) a swelling of the wood fibres in such a way that the wood structure is opened up, so that diffusion not only of sodium hydroxide but also of sodium chloride is greatly increased over the rate for sodium chloride into untreated chips; (ii) removal from the wood of resins, fats and other substances, which may be so distributed as to block passages through the cell walls which sodium hydroxide opens up by dissolving these substances.

TABLE VI

EFFECT ON RATE OF DIFFUSION OF TREATING CHIP WITH SEQUENCE OF DIFFERENT ELECTROLYTES

—	$T_{\frac{1}{2}}$, hr.	
	Chip No. 1	Chip No. 2
1st NaCl diffusion	24.5	23.0
2nd NaCl diffusion	22.0	24.5
1st NaOH diffusion	—	21.0
3rd NaCl diffusion	32.5	31.0
2nd NaOH diffusion	27.5	Over 30

If swelling is the explanation it would be expected that treating wood with sodium hydroxide of different concentrations should affect the increase in the rate of diffusion of sodium chloride to different extents. Six 2.5-cm. chips were impregnated with water and the rate of diffusion of sodium chloride into each chip was measured twice. Four of these chips were allowed to come to sorption equilibrium with sodium hydroxide of concentrations 1.4, 2.9, 6.2 and 10 molar respectively. After allowing the alkali to diffuse out of each chip, the rate of diffusion of sodium chloride was again measured twice. The fifth chip was placed in alcohol for several days and then in ether for five to six weeks. The chip was again placed in water and subjected to a vacuum to assist in removing the ether. The sixth chip was not used. The results of these experiments are given in Table VII.

TABLE VII

EFFECT OF PRETREATING WITH SODIUM HYDROXIDE OF VARIOUS CONCENTRATIONS ON RATE OF DIFFUSION OF SODIUM CHLORIDE INTO CHIPS AT 25° C.

Chip No.	$T_{\frac{1}{2}}$, min. (before treatment of chip)	Treating reagent	$T_{\frac{1}{2}}$, min. (after treatment of chip)
1	185 190	1.4 *M* NaOH	110 120
2	155 180	2.9 *M* NaOH	105 110
3	165 185	6.2 *M* NaOH	95 95
4	190 190	10 *M* NaOH	95 110
5	160 170	Alcohol and ether	— 170
6	205 205	—	— —

The experimental accuracy does not appear to be such that it is possible to distinguish between the different

concentrations of sodium hydroxide as regards their influence on the rate of diffusion of sodium chloride. It is rather surprising that concentrations between 1.4 and 10 *M* gave practically the same result. Only 0.3% of material was extracted from the chip soaked in ether, and the rate of diffusion of sodium chloride was unchanged. No conclusion can be drawn, therefore, whether the rate of diffusion would be increased by removing the fats and resins completely from the wood. More work will be necessary to explain definitely the action of sodium hydroxide on wood, whereby the rates of diffusion of sodium hydroxide and sodium chloride are increased in the lateral direction.

The results of the experiments at room temperature may be summed up as follows. In the longitudinal direction of black spruce heartwood, the three electrolytes diffuse at rates relative to each other in the order which would be expected from theoretical considerations—*i.e.*, hydrochloric acid the most rapidly, and sodium hydroxide and sodium chloride at nearly the same rates. In the lateral direction of the wood, sodium hydroxide diffuses the most rapidly because of its action on the wood, while sodium chloride and hydrochloric acid diffuse in the expected order of relative rates. The action of sodium hydroxide on the wood also increases the rate of lateral diffusion of sodium chloride to a degree similar to that of sodium hydroxide, and decreases the rate of longitudinal diffusion of both sodium hydroxide and sodium chloride.

Diffusion of Water into Air Dry Wood

The time required for an air dry chip, completely immersed in water, to sink was used as a measure of the relative rates of diffusion of water into different chips. The chips were of the same weights as those used in the experiments on the diffusion of electrolytes. Three series of experiments were carried out under the following conditions:—

(1) Open grained wood of about 15 annual rings per inch and a density of 0.40 of oven dry wood–at room temperature.

(2) Open grained wood of density 0.40 of oven dry wood —at 50° C.

(3) Close grained wood of 40-60 rings per inch and a density of 0.55 of oven dry wood–at room temperature.

The results of these experiments are given in Table VIII and are shown plotted in Fig. 5. The worst shape of chip for water diffusion, as indicated by the curve at 50°C., is shown in Fig. 3.

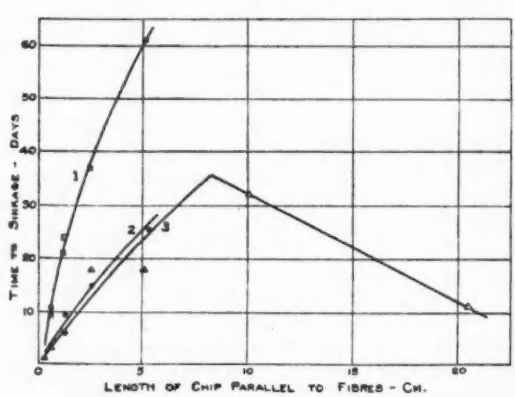

FIG. 5. *Diffusion of water into air dry chips of black spruce. 1, Open grained wood at 20° C.; 2, close grained wood at 20° C.; 3, open grained wood at 50° C.*

The data show that (i) raising the temperature from about 20 to 50° C. more than halved the time of sinkage, and (ii) the open grained wood required twice as long to sink as the close grained wood. A rise in temperature may cause three effects: *(a)* a decrease in the solubility of air in water, *(b)* more rapid diffusion of dissolved air molecules out of the chip, and *(c)* expansion of the air in the chip, which assists in its removal. Apparently the last two are predominant. The effect of the density of the wood is what would be expected, since a dense chip requires less water to diffuse into it before its density becomes greater than that of water, than is the case with less dense wood.

TABLE VIII

TIME REQUIRED FOR AIR DRY CHIPS TO SINK (T_s) IN WATER

Open grained wood at room temperature		Open grained wood at 50° C.		Close grained wood at 20° C.	
Chip length, cm.	T_s, days	Chip length, cm.	T_s, days	Chip length, cm.	T_s, days
0.64	11	0.32	1	0.76	4
0.66	9½	0.66	3	1.37	9½
1.27	24	1.29	6½	1.37	6
1.27	21	2.56	18	2.69	15
2.54	37	5.08	18	5.34	25½
5.13	61	10.1	32	—	—
—	—	20.5	11	—	—

The times required for sinkage obtained in these experiments with black spruce at room temperature are considerably greater than the values found by Richardson and Maass (1) for white spruce. The difference in results for these two varieties of spruce may be due largely to a difference in density of the wood.

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THE CAUSES OF THE CYTOLOGICAL RESULTS OBTAINED IN SPECIES CROSSES IN WHEAT[1]

By W. P. Thompson[2]

Abstract

There are several possible causes of the absence or low frequency of many chromosomal and genetic types in crosses between 42- and 28-chromosome species of wheat. The actual effects of these possible causes are:

1. Pre-gametic causes — effect small. Among pollen grains which develop normally all chromosomal types are found but not quite in theoretical proportions; those with chromosome numbers intermediate between the 14 and 21 of the parents are somewhat deficient. Intermediate numbers are more abundant among retarded grains.
2. Gametic
   (a) Male
      (1) Outright abortion of pollen grains — 5 to 10%.
      (2) Retardation of development — 25 to 30%.
      (3) Failure of pollen germination — the above 25 or 35%, plus probably as much more.
      (4) Competition and selective fertilization — impossible to determine accurately but probably some effect.
   (b) Female — very little. Apparently nearly all female gametes are capable of functioning but 50% usually remain unfertilized.
3. Endospermic — abortion and abnormal development cause important effects particularly in relation to female gametes but they cannot be separated completely from possible direct embryonic effects.
4. Embryonic — about half the embryos abort before the seed is ripe and at least half the F_2 seeds usually fail to germinate. These are in part and may be wholly endospermic effects.

The gametic and endospermic influences are such as to reduce the proportion of plants with chromosome combinations intermediate between those of the parents.

The Problem

The chief genetic results of crossing *vulgare* (42-chromosome) wheats with emmer types (28 chromosomes) may be stated briefly as follows: A large proportion of the F_2 and an increasing proportion in later generations possess the combination of characters found in one or the other of the parental types. In comparison with expectations based on varietal crosses, there are relatively few plants showing various combinations of the numerous characters which distinguish the parents. Some plants do resemble one species in one or a few respects and the other parent in other respects. But in general the proportion with various recombinations of characters is far below Mendelian expectations.

Underlying these genetic results is a corresponding set of cytological findings. Most of the F_2 plants have one or the other of the parental chromosome numbers or some number approaching these. There are very few plants with chromosome numbers nearly intermediate between those of the parents, in comparison with expectations based on the functioning of all types of reproductive cells and the development of all types of embryos.

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Contribution from the Department of Biology, University of Saskatchewan, Saskatoon, Canada, with financial assistance from the National Research Council of Canada.
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The cytological results become still more striking when the mating capabilities of the chromosomes are determined (2, 3). In this respect it is found that the plants fall into two groups, (a) those with 14 pairs capable of mating (the number in the emmer parent) plus from 0 to 7 single unmated ones; and (b) those with more than 14 pairs, all such plants having enough single chromosomes in addition to make the total of mated and unmated 21 (the number of pairs in the *vulgare* parent). If, for example, there are 17 pairs in any F_2 plant, there are also four unmated single chromosomes (not 3, 2, 1, 0, or 5). Kihara (3) first showed that those in Group (a) tend to revert in later generations to the condition with 14 pairs only (no univalents), whereas those in Group (b) tend to revert to the condition with 21 pairs. A large number of conceivable combinations such as 15 pairs plus 0 to 5 singles, 16 pairs plus 0 to 4 singles, etc., very seldom appear, and the rare plants which possess such combinations are weak and sterile.

Any one of several conceivable causes might be responsible for these results in whole or in part. For example, at the second reduction division in F_1 all of the seven unmated *vulgare* chromosomes might tend to go to one pole and none to the other. Or certain kinds of gametes or zygotes might be inviable owing to unbalanced or unfavorable chromosome conditions. Furthermore the unbalance might express itself in various ways and at various stages in the life cycle. In the following pages an attempt is made to determine which of the possible causes produce any actual effect and what the exact effect is. Various investigators have published data bearing on the influence of particular causes. The conclusions from these scattered data are assembled together with certain unpublished observations. The different possible influences will be treated in the order in which they would operate during the life cycle.

I. Pre-gametic Causes

It is conceivable that the extra seven *vulgare* chromosomes which remain unmated at the first meiotic division do not segregate at random to the poles of the cell at the second division. If all seven should tend to go to one pole and none to the other the resulting gametes would tend to have 14 + 7 or 14 + 0 chromosomes. A very similar situation actually exists in rose hybrids (1). If it occurs in wheat it would largely account for the results which are to be explained, particularly the low frequency of plants with intermediate numbers.

With this possibility in mind Thompson and Armstrong (8) determined the chromosome numbers in many young pollen grains in order to decide whether grains with numbers intermediate between 14 and 21 are actually formed in expected proportions. This was done by direct counts at one of the two divisions which take place within the pollen grain to produce the male gametophyte.

The first counts were naturally made in stamens in which a large proportion of the pollen grains were actively dividing. The results are given in the first row of Table I. It will be observed that there is a small deficiency of grains

with intermediate numbers in comparison with the theoretical. This is shown graphically in Fig. 1. When it was found later that many of the F_1 grains are retarded in development, it was thought that the deficiency might be due to retardation of those with intermediate numbers. Stamens were therefore studied in which many of the grains had already divided, and only retarded ones were at the division stage. The results are given in the second row of Table I. It will be observed that they show no deficiency in the intermediate classes but rather a slight excess; but in view of the small number (40) studied it is doubtful whether the frequency distribution of retarded grains differs significantly from the theoretical. And since only about 30% of all grains are retarded in development, it appears that the retarded grains cannot entirely make up the deficiency of those with intermediate numbers which was found among those developing normally. All the data available therefore indicate a small deficiency of grains with intermediate numbers. But this deficiency is slight in comparison with that among grains which function and produce offspring, as shown in the next section (see Fig. 1).

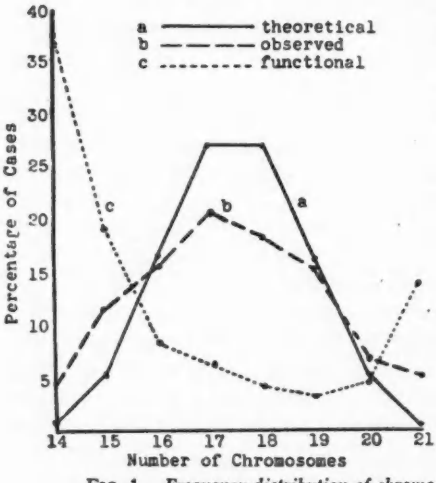

FIG. 1. *Frequency distribution of chromosome numbers in F_1 pollen grains; a, theoretical; b, observed in unretarded grains; c, functional.*

TABLE I

PERCENTAGES OF F_1 POLLEN GRAINS WITH VARIOUS CHROMOSOME NUMBERS

—	Chromosome numbers							
	14	15	16	17	18	19	20	21
Direct counts on normal grains	4.2	11.7	15.3	20.7	19.0	16.4	6.9	5.8
Direct counts on retarded grains	0.0	2.5	12.5	30.0	35.0	15.0	5.0	0.0
Functional grains	27.7	19.3	8.8	7.0	4.4	3.5	5.2	14.0
Theoretical	0.8	5.5	16.4	27.3	27.3	16.4	5.5	0.8

A subsidiary pre-gametic influence is the loss, through lagging, of univalent *vulgare* chromosomes at the meiotic divisions. Thompson and Hollingshead (10) found that in F_1 the approximate loss is one chromosome for every two pollen grains. Watkins (11) showed that a comparable loss occurs in 37-chromosome hybrid plants. The loss of chromosomes reduces the proportion of gametes with numbers higher than 14, and causes an excess of offspring with the lower numbers. This excess is reported by all investigators.

II. Causes Affecting the Gametes

It has frequently been suggested that one of the causes of the general cytological results is the failure to function on the part of the reproductive cells with intermediate chromosome numbers. In order to test this possibility Watkins (12), Sax (6) and the writer (9) independently undertook studies to determine the chromosome numbers of gametes which are capable of functioning. This was done by determining the chromosome numbers in plants which resulted from backcrossing the F_1 with the parents. The results of the different authors are in substantial agreement. Some of the writer's are given in Table I and are represented graphically in Fig. 1. Similar results have recently been published by Kihara (5).

It is clear that the great mass of pollen grains with intermediate numbers must have failed to produce offspring. The curve which represents the theoretical frequency distribution of the various types of pollen grains must be inverted to produce the curve for the grains which actually functioned.

The results for female gametes were similar but a larger proportion with intermediate numbers functioned than in the case of the male. Kihara (5) has recently stated that when F_1 is backcrossed with emmers, the results are nearly the same for female gametes as for male but, when it is backcrossed with *vulgare*, eggs with intermediate chromosomes function in nearly the expected proportions.

The inability of the great majority of the pollen grains to produce offspring may be due to several causes. These will now be considered.

(a) Death of Pollen Grains

A number of observers have reported that many of the mature F_1 pollen grains entirely lack protoplasm and that others have very little. The percentage of such grains is usually given as from 10 to 15. It is to be noted that there are various gradations between grains which are completely empty and those which appear perfectly normal, and that it is therefore impossible to draw a definite line between those which are clearly capable of functioning and those which obviously are not. In any case 10 to 15% is far less than the deficiency of functioning grains as determined by chromosome counts on backcross plants.

(b) Retardation of Development

Normally developing pollen grains of wheat enlarge greatly a short time after the completion of the meiotic divisions. This causes the presence of a large vacuole, the cytoplasm becoming restricted to a thin peripheral layer. The cytoplasmic layer then gradually thickens until the vacuole completely disappears some days before maturity. The first division of the pollen nucleus takes place while the vacuole is still large, and the second (the products of which become the sperms) occurs after the vacuole has disappeared.

In the F_1 all grains develop normally until the large vacuole is present (Thompson and Armstrong (8)). In a small percentage no further develop-

ment takes place; the cytoplasm not only fails to increase but gradually disappears. These are the ones which will be devoid of contents when the stamen is mature. Most of them can be recognized at the time the normal grains are undergoing the first gametophytic division.

In other grains the growth of the cytoplasm is slow. These lag farther and farther behind the normal. In different grains there are various rates of cytoplasmic increase and many seem to cease developing entirely at various stages. At the time when the first division is occurring in the normal grains only about 60% have the normal amount of cytoplasm, 25 to 30% show some degree of reduction, 6 to 12% have very little and about 1% are quite empty. By the time the stamen is mature the percentage of empty grains has risen to about five, while that of grains with a reduced amount of cytoplasm has decreased slightly.

There is a corresponding retardation in nuclear development which is evident at all stages. For example, when the normal grains have three nuclei many others have not yet divided once, and still more have only two nuclei. At maturity of the stamen, when normal grains have two sperms and a tube nucleus, about 5% are quite empty, 5% have only one nucleus, 10 to 15% have two, and another 10 to 15% have three nuclei but have not yet organized sperms. The grains with the retarded nuclear development are for the most part those with less than normal cytoplasm, although a small percentage which appear normal in cytoplasmic content have only two nuclei or no sperms.

It was shown in a previous section that pollen grains which are retarded in development are more likely to have chromosome numbers intermediate between 14 and 21 than are those which develop normally. This is evident from the data given in Table I. Presumably those which never divide at all, including those which lose their cytoplasmic contents, also have intermediate numbers.

(c) Pollen Germination

The abnormalities described in the last section leave 60 to 70% of the pollen grains in mature F_1 stamens apparently normal in cytoplasmic and nuclear development. About 10% are either entirely empty or have very little cytoplasm with a single nucleus and are evidently incapable of functioning. The remaining 20 or 30% show various amounts of cytoplasm and various stages of nuclear development. It seems probable that they also would be unable to germinate. Moreover it is possible that some of the grains which appear normal may be injuriously affected by chromosome conditions in ways which produce no visible effect. Tests of the germinating capacity of the pollen were therefore undertaken.

Watkins (11) has studied the germination of F_1 pollen of *vulgare* × *turgidum* and found that from 5 to 30% germinated depending on conditions.

Thompson and Armstrong (8) found it impossible to secure reliable results on the germination of any kind of wheat pollen in the laboratory. They were therefore compelled to make their observations on pollen in contact

with stigmas. It was found that in conditions in which 80 to 90% of parental pollen germinates none of the grains with any reduction in the amount of cytoplasm or with retarded nuclei are able to germinate. Moreover a large percentage of the apparently normal grains also fail to germinate. Altogether not more than 15% of all grains germinated on F_1 stigmas in our experiments. It must not be concluded that under entirely natural conditions the germination would be as low as this but it is evidently considerably lowered even for normal looking grains in comparison with parental pollen.

(d) Competition Between Gametes and Selective Fertilization

Pollen grains with certain chromosome numbers may be able to develop and germinate but their tubes may be handicapped, by slow growth, in competition with grains which have more favorable chromosome combinations. This possibility cannot be tested directly owing to the nature of the feathery, much-branched wheat stigma, which is attached directly to the ovary. But from what is known of similar situations in other plants (for example $n + 1$ pollen in *Datura*), it may be important. The only direct evidence bearing on the point in wheat is that, at 10 hr. after pollination, one in every four of the germinated F_1 pollen grains has developed only so far as to protrude the tip of the tube, the rest of the germinated grains having by this time produced well developed tubes. On the other hand among parental pollen grains only 1 in 14 is so retarded.

Kihara (5) has recently published results which indicate that when F_1 plants receive emmer (14-chromosome) pollen, it is chiefly 14- to 16-chromosome eggs which function and produce offspring, whereas when the same F_1 plants receive *vulgare* (21-chromosome) pollen it is chiefly 17- to 21-chromosome eggs which produce offspring (Table II). A strong selective effect is thereby indicated. It must be remembered, however, that when F_1 is backcrossed to *vulgare* the germination of the seeds is poor, and that the low frequency of backcross plants from 14- to 16-chromosome eggs may be due, in part at least, to incomplete germination. The writer's results, involving only a small number of plants, did not indicate such a selective action.

Kihara also stated that when emmer plants receive F_1 pollen it is chiefly 14-chromosome pollen grains which function and produce offspring, whereas when *vulgare* plants receive the same F_1 pollen 21-chromosome grains function as frequently as those with 14 (Table II). But again it must be remembered

TABLE II

FREQUENCY OF F_1 GAMETES WITH VARIOUS CHROMOSOME NUMBERS, WHICH PRODUCED OFFSPRING IN BACKCROSSES. (DATA FROM KIHARA (5))

Chromosome number	14	15	16	17	18	19	20	21	Total
$F_1 \times$ *vulgare*	4	3	2	6	9	5	2	0	31
$F_1 \times$ *durum*	37	16	15	4	1	3	1	4	81
T. vulgare $\times F_1$	6	7	2	2	4	2	1	8	32
T. durum $\times F_1$	12	8	2	0	1	0	0	0	23

that in emmer × F_1 the germination of the seeds is poor and the low frequency of plants from 21-chromosome pollen grains may be due, in part at least, to poor germination. It is also conceivable that in this type of backcross (parents × F_1) the 14-chromosome tubes grow better in 28-chromosome stigmas and 21-chromosome tubes grow better in 42-chromosome stigmas (14). If that is the case, 14-chromosome grains would function most frequently when emmer is the female parent used and 21-chromosome grains would function better when *vulgare* is the parent. Opposed to this conception is the fact that in the reciprocal type of backcross (F_1 × parents) there is a similar difference in the eggs which function depending on the parent used. But in this case the nature of the stigma can play no part since all stigmas are alike (F_1).

(e) Abortion of Female Gametes

All investigators agree that less than 50% of the F_1 flowers set seed when they are self-pollinated and the percentage often falls as low as 15. This has been regarded as the result of the abortion of embryo sacs corresponding to the abortion of pollen. Earlier reports of the results of backcrossing F_1 to the parents would lead to the same conclusion. On the other hand Watkins (11) reported that F_1 flowers which receive parental pollen set seed in almost as high a proportion of cases as parental flowers in crosses between pure lines (87% for F_1; 90% for pure lines). This would indicate that almost every female gamete is able to function successfully. This result is confirmed by Kihara (5) who obtained up to 90% seed setting on F_1 when the work was done very carefully. It therefore appears well established that there is very little abortion of embryo sacs and that low seed setting when F_1 is selfed is due to the failure of fertilization or to something which happens subsequent to fertilization.

This conclusion is supported by Kihara's (4) microscopic examination of ovules collected two or three days after the flowering time. He found that less than 2% of the embryo sacs were degenerate. Although only 41% contained embryos, the remaining 57% were healthy and had apparently escaped fertilization. Watkins (11) has reported similar findings for certain F_3 plants which were almost as sterile as F_1.

The abortion of female gametes is therefore not an important factor in the general cytological situation.

III. Causes Affecting the Endosperm

It is well known that the seeds borne on interspecific hybrids are commonly small and wrinkled or shrivelled. In such cases the amount of endosperm is usually less than in the parent seeds and it is almost invariably abnormal in appearance or texture.

Watkins (12) and Thompson and Cameron (9) showed that in wheat there is a correlation between the abnormal endosperm condition and chromosome numbers. If the 14-chromosome parent is female the F_1 endosperm is

wrinkled, but in the reciprocal cross the endosperm is plump. The chromosome numbers in the endosperm are quite different in these two reciprocal crosses, owing to the fact that the tissue develops from a fusion of one male and two female nuclei. When the 14-chromosome parent is female the wrinkled endosperm has only one set of the extra seven chromosomes contributed by the male *vulgare* gamete (49 in all); in the reciprocal cross it has two sets of the seven (56 in all).

Thompson (7) carried the study further and determined the chromosome conditions in a large number of backcross and F_2 seeds of various degrees of shrivelling. He found that the endosperm is wrinkled or shrivelled whenever it is (a) haploid for all or many of the extra seven *vulgare* chromosomes, or (b) diploid or triploid for only a part of the seven. The farther the chromosome situation departs from the normal complete absence or complete triploidy of the seven *vulgare* chromosomes the severer is the shrivelling. A doubled or tripled condition of part of the set of seven causes a lack of balance which prevents normal endospermic development.

Such abnormal endospermic conditions must occur precisely in those seeds from which the missing chromosomal types of plants would have to develop. For example, a plant with 18 pairs of chromosomes (and no univalents) would have to develop from a seed which had four of the extra seven represented three times in its endosperm and the remaining three quite unrepresented. This highly unbalanced chromosome condition would cause the abortion of the endosperm. Other missing chromosomal types would have to develop from seeds with similar unbalance in the endosperm although, of course, the unbalance would not always be so extreme.

In extreme cases it may be expected that the endosperm could not develop at all and consequently the seeds could not be formed. In the absence of microscopic studies it is impossible to say in what proportion of cases this occurs. In less extreme cases the endosperm would develop slowly or abnormally and would be shrivelled. The shrivelling lowers the germination and thus eliminates the chromosomal types of zygotes involved. There are many published data on the poor germination of hybrid seeds in these crosses. Thompson and Cameron (9) classified their seeds according to the degree of wrinkling and showed the expected high correlation between wrinkling and poor germination. In backcrosses the percentage of seeds which germinate depends on the direction in which the backcross is made; in some cases it is only 35%. In direct crosses probably never more than 50% of the seeds formed on F_1 plants by self pollination are able to germinate.

It might be supposed that the elimination of gametes at pre-fertilization stages as described in previous sections would reduce the possible endospermic effect to small proportions, since few gametes might be left to eliminate. But it must be remembered that female gametes are much less affected than the male by pre-fertilization influences; nearly all of them, in fact, are apparently able to function. And the endospermic influence would be particularly

effective in relation to female gametes, since the female contribution (and therefore the unbalancing effect of any extra chromosomes which it contains) is doubled in the endosperm.

IV. Causes Affecting the Embryos

The unbalanced chromosome condition which injuriously affects the endosperm may also affect the embryo independently of the endosperm. It is to be expected, however, that the triploid endosperm would be more injuriously affected than the diploid embryo since the unbalance would be greater. In agreement with that expectation is the fact that shrivelled grains, if they germinate at all, may produce perfectly healthy plants. If there is a direct effect on the embryo it would be difficult to distinguish from the effect produced through the abnormal endosperm except perhaps at early stages.

Kihara (4) has provided some data on the abortion of embryos. In a microscopic study of ovules collected two or three days after pollination he found that 41% of the F_1 embryo sacs contained embryos. But in fully comparable mature ears only 16% of the flowers had produced seeds. Therefore more than one-half of the embryos had aborted. This means that approximately 25% of all flowers are sterile because embryos which are formed in them fail to develop. To this amount of zygotic elimination must be added that which is involved in failure of the seeds to germinate.

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THE GENERA *HALICTUS* AND *ANDRENA* IN WESTERN NOVA SCOTIA[1]

By C. E. Atwood[2]

Abstract

This paper deals principally with the classification of the bees of the genera *Halictus* and *Andrena* collected during a five-year project on the pollination of the apple in the Annapolis-Cornwallis Valley, Nova Scotia. Keys for the separation of the species concerned are given, together with figures of the eighth and ninth abdominal sterna of the males, which were found very useful in separating related species. One new species, *Andrena kalmiae* Atwood, and the true male of *A. ceanothi* Vier., are described, and a re-description of *Halictus arcuatus* Rob. is given, including a summer form which is presumably sterile. The taxonomic section is prefaced by brief notes on economic importance and biology of the genera.

Introduction

The study of the two genera of bees, *Halictus* and *Andrena*, as represented in western Nova Scotia was begun in connection with an investigation of the problem of apple pollination in the Annapolis-Cornwallis Valley, conducted in the seasons 1928-1932 by the Department of Agriculture, Ottawa, the work being under the immediate direction of Dr. W. H. Brittain.

When counting the numbers of various insects which visited apple bloom, it was clear that the bees of the genera *Halictus* and *Andrena* played a leading part in apple pollination. Accordingly, biological and taxonomic studies appeared necessary for intelligent interpretation of such counts and presentation of the results. It was eventually decided to include in the present study all the species of these genera found in the region investigated, whether taken on apple or not, in order to make the list as complete as possible. The results of studies on the material collected during the summers in which the project was carried on are presented herewith. A considerable number of specimens of other genera of bees, and other insects, were also taken; these have been placed in the National Collection at Ottawa and await further study. The list of *Halicti* and *Andrenae* cannot be considered as complete for the province. Several species reported from there have not been taken by the writer. Some of these reports were based on incorrect identifications. It is hoped, however, that the keys, descriptions, and drawings given will enable anyone to identify the great majority of species of these genera that may be taken in Nova Scotia.

Economic Importance

In the apple growing districts of Nova Scotia, four genera of bees are chiefly concerned with the pollination of the bloom and consequent production of the crop. Three of these, *Bremus*, *Halictus*, and *Andrena*, are native,

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Contribution from the Entomological Branch, Department of Agriculture, Ottawa and the Department of Biology, University of Toronto. This paper constitutes part of a thesis submitted in May, 1933, to the graduate faculty of the University of Toronto, in partial fulfilment of the requirements for the degree of Master of Science in Agriculture.
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while the fourth is represented by the domesticated *Apis*. Owing to the losses caused to beekeepers by spraying and dusting for orchard pests, very few honeybees are kept in the Annapolis-Cornwallis Valley at this time so that these insects are a negligible factor in the pollination of apple over most of this area. The evidence also seems to show that *Bremus* has decreased in numbers in the orchard region, and at present also plays a very small part in orchard pollination. Consequently, the other two groups are chiefly responsible for the pollination which takes place, as they seem to have suffered very little from poisoning. This is not an entirely satisfactory situation because these bees are more sensitive to temperature and light than *Bremus* and *Apis* and fly only on comparatively warm and sunny days, so that a long period of dull weather during bloom may result in lack of sufficient pollination unless honeybees are introduced. On the whole, however, their efforts must be considered successful to a large degree because the crops which are produced are the result of their activities. In addition to apple, these bees also act as pollinators for cherry, plum, pear, and the various smaller fruits such as raspberry, strawberry, and gooseberry, as well as numerous wild and cultivated flowers. Both from the economic and from the aesthetic standpoint their importance can hardly be overestimated.

Biology

The life histories and nesting habits of the genus *Andrena* have been studied in Europe by various entomologists. Perkins (5) gives an excellent account of some British species and their parasites. They are entirely solitary, each female making her own nest, although the holes may be very close together in favorable places. There may be two broods per year, but all the Nova Scotian species appear to have only one. This brood may appear in early spring, as in the case of *A. carlini*, or in the fall, as in *A. hirticincta*.

The burrows of those observed in Nova Scotia were generally constructed among grasses or other low herbage rather than on bare soil, and were rather difficult to find. They varied in length from a few inches to some two feet, being as a rule deeper on sandy soil. The pollen was stored in some cases as a pellet, in others as a very stiff paste of mixed nectar and pollen. Several species of *Nomada*, a genus known to be parasitic on *Andrena*, were taken in the region, but their relation to particular species of *Andrena* has not yet been traced. Nova Scotian bees of several genera are also attacked by *Strepsiptera*, *A. thaspii* being apparently most susceptible.

Although there has been very little written about the nesting habits of American *Halicti*, European species have attracted considerable attention. It has been generally agreed that the spring brood of *Halictus* consists of females only and that males do not appear until midsummer or later, but various opinions have been expressed regarding the details of the different broods. Fabre (2) concluded that the spring brood consisted of overwintered females who made the nests and laid the first eggs; that these were followed by a parthenogenetic brood of females; and that these laid eggs which gave

rise to a fall brood of males and females, the latter going into hibernation. The spring females were also considered to live until fall and to act as guardians over the cells provisioned by their daughters. Armbruster (1) stated that there were two parthenogenetic generations, the first producing a summer brood of females only, this again giving rise parthenogenetically to a fall brood of males and females. The latest work is that of Stöckhert (10), who differs from both of the foregoing. He found that the females of *H. malachurus* spend the winter in hibernation and emerge early in the spring, immediately beginning to clean out the burrow or to dig new ones. The number of summer broods differ; there may be one, two, or three. In the species which have three broods, there is a primitive type of social organization. The first eggs laid by the spring female develop into females which are smaller than their mother and often differently sculptured. These visit flowers and gather pollen and nectar to provision the nest cells while the original mother lays more eggs, of which some produce females, the others males. The summer brood never lay eggs and are never fertilized by males, and therefore correspond to the workers of *Bremus*. In the fall the mother, the males, and the sterile females die, while the fertilized fall females hibernate, several usually being found in one burrow.

The habits of the species observed in Nova Scotia seem to be very similar to those recorded for the German species. *H. zonulus* and *H. provancheri* appear to have only two generations. *H. rubicundus* appears to have a sterile brood of some six females. *H. arcuatus* and *H. viridatus* have the most highly organized social system, apparently quite similar to that of the three-brooded species noted by Stöckhert. They appear very early in the spring and begin making and provisioning their nests. *H. arcuatus* does not hibernate in its summer hole and therefore must dig a new nest, while *H. viridatus* may simply clean out the previous year's nest in which it has spent the winter. While most of the spring nests are occupied by a single female, many of them may contain two, three, or four females. It is remarkable that although *H. arcuatus* does not hibernate in its summer tunnel, two females have been found excavating a new hole together in May. In the case of *viridatus* several females are commonly found in the hibernation tunnel, but in spring one usually retains the winter hole while the others make new ones. This procedure is by no means invariable, however, as indicated above. When two or more females occupy the same hole, one is frequently seen standing guard at the entrance.

The first adults of the summer broods begin to emerge from the pupal state during the latter part of June; these are sterile females. The males do not appear until nearly a month later. It was not found possible to establish a definite line between the spring females and the sterile second generation as regards external characters, but in *H. arcuatus* a number of summer females are smaller and have a proportionately longer dorsal space on the propodeum, as well as slightly different sculpturing. In *viridatus* a marked difference in size is often seen among the inhabitants of a single nest; differences of puncta-

tion occur also, but none of these have been definitely associated with any particular brood. Stöckhert's observations were checked by dissection of the female reproductive system. This has not been done as yet with the Nova Scotian species under consideration, and would undoubtedly throw additional light on the subject. The evidence would seem to indicate, however, that the two last-mentioned species show an elementary social system, with a primitive worker caste, and some degree of division of labor and co-operation among the inhabitants of a nest.

Taxonomy

The taxonomic literature on these two genera is scattered through many journals and books and is written in several languages. Most of the earlier attempts to classify the bees were made by Europeans; among the important contributions being those of Schmiedeknecht (7), Friese (3), and Smith (8, 9.) The latter described many of the North American species but his descriptions are usually too vague to make exact identification certain without comparison with the types. The others have proposed classifications of the bees as a whole, each differing from the others in his ideas as to the relationships between the various groups. In America, Cresson, Ashmead, and Robertson have contributed many important papers on the *Apoidea*, and Robertson and Viereck have proposed schemes for the division of *Halictus* and *Andrena* into subgenera.

Because of the large number of species, the variability of characters, and the inadequate descriptions of the earlier writers, the nomenclature for these genera is still in a very confused state and must remain so until a careful revision of the North American species is completed. For this reason, a paper dealing with a local fauna must contain some names which are more or less tentative, and this is true of the present list.

Because of the slight and inconspicuous characters distinguishing some species, it is often very difficult to indicate differences in a key or verbal description. Morice (4) in 1899 pointed out that the genital armature and the eighth ventral segment in *Andrena* were of considerable value in distinguishing closely allied European species of that genus. These characters have been examined in the Nova Scotian species under consideration, and an attempt made to illustrate them by semidiagrammatic drawings. In many cases examination of these is unnecessary for the separation of the species mentioned in this paper, but a drawing of such a character defines a species in a more precise way than the comparative differences given in keys, and makes it possible to distinguish it from a related species, no matter where the latter may occur.

In some cases it has been possible to secure only one sex of a species, and consequently the missing one does not appear in the keys. Also, several unidentified species have been omitted completely as they are represented by only one or two specimens which could not be recognized from descriptions

or by comparison. They may be new species but it is better to wait until more material is secured, so that a series is available for study. In the meantime they will be deposited in the National Collection at Ottawa.

One of the chief difficulties in dealing with these bees is the proper association of sexes, as the males and females are often extremely unlike each other. The securing of nests and their inhabitants, the taking of couples *in copula*, and data on time of appearance and flowers visited may help to solve this difficulty, and a special effort was made to secure as much information of this type as was possible. The taking of populations from nests also permits the limits of variation within the species to be studied; the lack of study of this subject has led to the naming of many species on insufficient grounds.

In regard to the synonymy of the species dealt with, the writer is greatly indebted to Miss Sandhouse, who has compared some of the material with European specimens and established their identity.

Halictus Latreille

Key to Species

Females

1. Portion of cubital vein between second and third transverse cubital veins not obsolescent; abdomen with heavy apical fasciae of appressed pubescence 2
   Portion of cubital vein between second and third transverse cubital veins obsolescent; abdomen with fasciae basal, indistinct, or absent 3
2. Head, thorax, and abdomen black; propodeum rugulose; mesonotum and abdomen closely punctate ..... *rubicundus* (Christ.) Kby.
   Head, thorax, and abdomen greenish; clypeus purplish; propodeum, mesonotum, and punctate abdomen as above ..... *provancheri* D.T.
3. Head and thorax greenish or bluish 13
   Head and thorax black 4
4. Mesonotum and abdomen very closely punctate, lustreless, usually with a bluish bloom; second, third and often fourth abdominal terga with heavy basal fasciae of appressed pubescence; posterior edges of terga thick; propodeum rugulose or granular, roughest at sides; hind tibial spur with eight or more short, rather broad and blunt teeth 5
   Mesonotum and abdomen polished and shining between punctures; teeth of tibial spur either fine serrations, or fewer in number than above, and long; posterior edges of terga thin 6
5. Propodeum smooth at posterior edge of dorsal space ..... *coriaceus* Sm.
   Propodeum rough at posterior edge of dorsal space ..... *athabascensis* Sandh.
6. Head conspicuously short and broad; teeth of tibial spur fine serrations; propodeum short, coarsely rugose; first abdominal tergum finely and sparsely punctate; complete or interrupted basal fasciae usually present ..... *arcuatus* Robt.
   Head not conspicuously short; clypeus at least slightly produced 7
7. Propodeum smooth at posterior edge of dorsal space; first abdominal tergum very finely and sparsely punctate; about four long tibial teeth 8
   Propodeum rough (rugose or granular) from base to posterior edge of dorsal space 9
8. Second and third abdominal terga without patches of white pubescence on sides; mesonotum very finely and closely punctate ..... *foxii* Robt.
   Second and third abdominal terga with patches of white pubescence on sides; mesonotum with punctation slightly more coarse than above ..... *macoupinensis* Robt.
9. First abdominal tergum impunctate; mesonotum strongly punctate; propodeum coarsely rugose, dorsal space bounded posteriorly by a salient rim; first recurrent vein practically continuous with second transverse cubital vein; tibial spur with about six long teeth ..... *pectoralis* Sm.
   First abdominal tergum at least finely punctate 10

10. First abdominal tergum strongly punctate; second, third and usually fourth with broad, complete or incomplete basal fasciae; propodeum coarsely rugose..... 12

First abdominal tergum finely and sparsely punctate; fasciae very thin, or on sides of terga only; propodeum rather finely rugulose or granular..... 11

11. Abdomen not fasciate or with small incomplete fasciae at sides; tibial spur with about six rather long sharp oblique teeth; rugae of propodeum rather close together; posterior edge of dorsal space decidedly roughened.....*rufitarsus* Zett.

Abdomen with thin apical fasciae of sub-erect, pale rusty hairs, usually complete on one or more terga; propodeum long, rugae rather far apart; posterior edge of dorsal space almost smooth; tibial spur with about four long, pointed oblique teeth.....*quebecensis* Cwfd.

12. First abdominal tergum regularly and closely punctate, rather dull; tibial spur with six or more conspicuous stout teeth.....*leucozonius* (Schrank.)

First abdominal tergum sparsely punctate toward centre, more closely toward sides, polished and shining; tibial spur finely serrate.....*zonulus* Sm.

13. Thorax and abdomen yellowish green; mesonotum distinctly and very closely punctate; first abdominal tergum finely and closely punctate; second, third and fourth terga practically covered with appressed, felt-like, yellowish pubescence, propodeum closely rugulose.....*pilosus* Sm.

Abdomen black, or with a faint brownish tinge; pubescence somewhat more sparse and less felt-like than above..... 14

14. Mesonotum coarsely punctate..... 15

Mesonotum finely but distinctly punctate, abdomen black, shining.....*viridatus* Lov.

15. Abdomen blackish opaque, posterior margins of terga not conspicuously testaceous, wings yellowish.....*cressonii* Robt.

Abdomen brownish, shining, posterior margins of terga broadly testaceous; wings clear.....*nubilus* Lov.

Males

1. Abdominal segments with apical fasciae; closely punctate; clypeus with a broad transverse yellow mark at apex; hind tibiae and tarsi mostly yellow; propodeum closely rugulose..... 2

Abdominal segments without distinct apical fasciae, at most a thin band of sub-erect hairs along apical margin..... 3

2. Head, thorax, and abdomen greenish.....*provancheri* D.T.

Head, thorax, and abdomen black.....*rubicundus* (Christ.) Kby.

3. Thorax, greenish, bluish or purplish; dorsal space of propodeum rugose; abdomen black or brownish..... 12

Thorax black; dorsal space rugose or rugulose, sometimes smooth at posterior edge of dorsal space..... 4

4. Anterior portion of clypeus flattened or concave, shining and polished, almost or entirely without hairs or punctures, a broad transverse yellow spot at apex; first abdominal tergum closely punctate..... 5

Anterior portion of clypeus transversely rounded, more or less punctate, and with a distinct covering of hairs; yellow spot present or absent..... 6

5. Tip of mandible when closed reaching practically to base of opposite mandible; face very broad; form robust; basal fasciae of abdomen mostly complete..*coriaceus* Sm.

Tip of mandible when closed reaching only about three-fourths of distance to base of opposite mandible; smaller, form less robust; basal fasciae mostly incomplete, tarsi reddish.....*athabascensis* Sandh.

6. Sixth sternum of abdomen with an entire and evenly rounded posterior margin; no conspicuous bands or tufts of hair on that segment..... 8

Sixth sternum with distinct bands or tufts of hair..... 7

7. Sixth sternum of abdomen with two prominent tufts of hair along its longitudinal axis. postero-lateral margin reflexed; face broad; first abdominal tergum sparsely punctured toward centre, more closely toward edges; posterior tarsi brownish.....*zonulus* Sm.

Sixth abdominal sternum with two dense converging bands of hair, which meet about half-way from apex to base, giving it a notched appearance; clypeus somewhat produced; first abdominal tergum evenly punctate; posterior tarsi yellow.....*leucozonius* (Schrank.)

8. Dorsal space of propodeum rugose, bounded posteriorly by an elevated and roughened ridge..... 9
   Dorsal space rugulose at base, smooth at posterior edge, without a sharp rim, clypeus with a pale yellow or whitish mark..... 11
9. Antennae not conspicuously longer than thorax, joint three about equal to joint four; clypeus black; mesonotum strongly punctate; propodeum with few rugae; abdominal terga with numerous short, light, sub-erect hairs.....*pectoralis* Sm.
   Antennae conspicuously longer than thorax, joint three not more than one-half as long as four; propodeum with numerous irregular rugae..... 10
10. Clypeus produced; mesonotum finely punctate; first abdominal tergum very finely and sparsely punctate; hind tarsi brownish.....*rufitarsus* Zett.
    Clypeus hardly produced; mesonotum and first tergum strongly punctate; hind tarsi whitish.....*arcuatus* Robt.
11. Form slender, conspicuously longer than thorax.....*foxii* Robt.
    Form not slender, antennae not conspicuously longer than thorax...*macoupinensis* Robt.
12. Head almost black, thorax dark purplish.....*consonus* Sandh.
    Head and thorax distinctly green or bluish..... 13
13. Clypeus with a yellow mark; mesonotum finely and closely punctate; distal end of posterior femora and both ends of posterior tibiae bright yellow; abdomen greenish.....*pilosus* Sm.
    Clypeus without a yellow mark; mesonotum not very closely punctate; abdomen black or brownish..... 14
14. Punctures of mesonotum sparse, coarse; face densely covered with white felt-like pubescence..... 15
    Punctures of mesonotum fine; face usually with sparse appressed hairs.....*viridatus* Lov.
15. Antennae black or dark brown, abdominal terga without a broadly testaceous margin.....*cressonii* Robt.
    Antennae light yellowish brown beneath; posterior margins of abdominal terga broadly testaceous.....*nymphaearum* Robt.

H. arcuatus Rob.*

H. arcuatus Robertson. Trans. Am. Ent. Soc. 20: 145; 1893.

Female

Black; head short and broad, clypeus coarsely, sparsely, and irregularly punctate, a very conspicuous fringe of yellowish hair on apex; mandibles blunt, red at tip, with a strong preapical tooth; face closely punctate, somewhat roughened, with sparse, whitish erect hairs, antennae black or dark brown, basal joint shining.

Mesonotum shining, strongly and regularly punctate, surface finely roughened, pubescence gray or light brownish, sparse except along edges; scutellum with a wide area along axis closely punctate and roughened, and a shining almost impunctate space each side, edges of sclerite closely punctate, hairs similar to those of mesonotum but longer; metanotum rough, mostly covered with appressed dull gray pubescence with long hairs over; dorsal space of propodeum shining, very strongly rugose, with about 15 longitudinal ridges, which extend to the posterior margin and make it very rough in the central area; posterior margin slightly rounded; lateral fringe of hairs thin; sides of propodeum striate around edges, smooth and tessellate in centre; wings slightly tinged with brownish, veins and stigma clear yellow testaceous, second submarginal cell nearly as long as third, tegulae brownish or nearly all black; legs black, brown, or reddish, tarsi reddish, pubescence gray, or yellowish toward apical joints, especially on inner side of tarsi; hind tibial spur with about six short, sharp, oblique teeth.

**A full description of this species is given in order to distinguish the spring from the summer form.*

First abdominal tergum polished and shining, finely and sparsely punctate, following segments more closely punctate, especially on bases; posterior borders of terga brownish testaceous; second, third, and usually fourth with patches of white appressed pubescence on sides, which may extend completely across segment or be missing altogether from one or more; third and fourth, and sides of first and second with sparse semi-erect yellowish or grayish hairs, fifth densely covered with yellowish or light brownish hairs about rima. Length 7-9 mm.

What appears to be a summer form of this species has been taken in great numbers on sumac (*Rhus*) and rose during July and August, and also from nests in the only community of this species which was found. It is smaller, about 6-7 mm.; the dorsal space of the propodeum is long, more rounded behind and more finely and irregularly rugose, almost reticulate, and the patches of appressed whitish pubescence on the abdomen are usually small, seldom present on the fourth segment and sometimes practically absent.

Male

Black; face broad, densely clothed with white, felt-like pubescence, clypeus with a more or less distinct pale yellow mark anteriorly, sometimes almost completely absent; antennæ very long, black or brown, with constrictions between joints; mesonotum like female; scutellum punctate all over, a rounded elevation on each side of longitudinal axis; metanotum closely rugulose, with sparse erect hairs only; propodeum shining, dorsal space very coarsely rugose, posterior space and sides more finely rugulose or reticulate, pubescence of thorax gray or brownish; wings clear hyaline, veins and stigma dark testaceous to brown; legs black, tibial spurs and first tarsal joint light yellow, the latter with a black or brown distal end, other tarsal joints black or brown with a varying amount of yellow at base; abdomen slender, black, shining, closely and finely punctate, with patches of white appressed pubescence on second and third segments. Length 7-8 mm.

The nearest eastern species to this is apparently *H. truncatus* Rob., from which it is distinguished by the punctate first abdominal segment.

180 females, 31 males, numerous other specimens exchanged. Hants, Kings, and Lunenburg counties, May 20 to August 23. Common, especially on Rosaceae and Compositae.

Andrena Fabricius

Key to Species

Females

1. Mesopleura with a conical or somewhat keel-shaped projecting process; clypeus strongly punctate with an upturned rim along its anterior edge ..... *persimulata* Vier.
   Mesopleura without such a projecting process 2
2. Facial line distinctly longer than transfacial line; facial fovea narrow; second tergum depressed posteriorly less than half of its length; first tergum sparsely punctate, minutely tessellate between punctures; pubescence mostly pale, anal fimbria brown ..... *bradleyi* Vier.
   Facial line shorter than transfacial line 3

3. Dorsal space of propodeum coarsely rugose, usually with distinct longitudinal rugae, sometimes almost reticulate, generally bounded posteriorly by a transverse ridge; third joint of antennae shorter than, or at most equal to, fourth and fifth together; mesonotum with strong clear-cut punctures, which stand out conspicuously from the minute tessellations between them; abdomen strongly and rather closely punctured 23

   Dorsal space of propodeum rugulose, or plicatulate at base, triangular, never with strong elevated ridges running from base to posterior edge, usually defined by an impressed line or absence of hair, and continued to a point on the posterior face; never separated from posterior face by a raised transverse ridge; third joint of antennae generally longer than fourth and fifth together; mesonotum with punctures partially obscured by the roughening between them 4

4. Hind tibiae and tarsi bright yellowish or ferruginous; abdominal terga distinctly punctate, strongly roughened; clypeus with a narrow impunctate space forming a raised line down its centre, this area tessellate ..... *wilkella* (Kby.) Ill.

   Hind tibiae and tarsi at most dull reddish brown 5

5. Hairs of tibial scopa dark brown or black 6

   Hairs of tibial scopa light gray to fulvous 10

6. Abdominal terga, except the apical two, without conspicuous long hairs 8

   Terga conspicuously clothed with long, more or less erect, hairs 7

7. Pubescence of head, thorax and dorsum of abdomen except anal fimbria yellowish, erect, dense; clypeus closely punctate with a narrow, roughened, median impunctate space ..... *hirticincta* Prov.

   Pubescence of mesonotum and at least the first two abdominal terga bright fulvous; that of face, cheeks, part of pleura and apical terga black or dark brown; clypeus sparsely punctate, median impunctate space wide, polished, shining *milwaukeensis* Graen.

8. Face, cheeks, and pleura without black or dark brown hairs; face coarsely punctate with a narrow shining impunctate space ..... *vicina* Sm.

   Face and cheeks with some dark brown or black hairs; pleura with a patch of dark brown or black hairs 9

9. Face with coarse irregular punctures, and a distinct median impunctate space *carlini* Ckll.

   Face with rather small regular punctures, no median impunctate space ..... *regularis* Mall.

10. Face with some black hairs; clypeus closely punctate with a narrow triangular or T-shaped median space; abdominal terga with long, silky, rather sparse gray hairs, not forming definite transverse bands ..... *frigida* Sm.

    Face without black hairs 11

11. Second, third, and fourth abdominal terga with complete apical fasciae of dense appressed ochraceous hairs; first tergum impunctate, tessellate, bare except for scattered hairs at base and sides 12

    Abdominal fasciae absent, incomplete, or formed of somewhat sparse, partly erect hairs 13

12. Wings clouded at tips; dorsulum tessellate ..... *nubecula* Sm.

    Wings not clouded at tips; dorsulum polished ..... *canadensis* D.T.

13. Distance from inner margin of eye to inner margin of facial fovea, along a transverse line through centres of antennal sockets, equal to or greater than one-half distance from inner margin of eye to outer edge of antennal socket 17

    Distance from inner margin of eye to inner margin of facial fovea less than one-half distance from inner margin of eye to edge of antennal socket 14

14. Process of labrum truncate at apex 15

    Process of labrum rounded at apex 16

15. Clypeus slightly produced, sparsely punctate except at base and lateral margins, with a distinct shining impunctate space; facial foveae nearly uniform in width; stigma and veins medium brown, second submarginal cell with sides subequal *novaeangliae* Vier.

    Clypeus convex, not produced, distinctly and somewhat closely punctate, roughened between punctures, no median impunctate space; facial foveae distinctly widened toward vertex; stigma and veins very dark brown, second submarginal cell distinctly longer than high, oblique ..... *algida* Sm.

16. Process of labrum arcuate, stigma and veins light brown; first recurrent vein received by second submarginal cell before its middle; clypeus sparsely punctate *vagans* Ckll.

    Process of labrum sub-triangular, rounded at apex, length equal to about one-half width of base; stigma and veins honey-yellow; first recurrent vein received by second submarginal cell beyond its middle; clypeus convex, closely punctate at sides, more sparsely toward middle with an irregular impunctate space *salictaria* Robt.

17. Process of labrum emarginate; clypeus strongly punctate, roughened between punctures, no median impunctate space; abdomen thinly subfasciate; first tergum impunctate ..... *lata* Vier.
Process of labrum not emarginate 18
18. Greater part of clypeus impunctate, polished, shining; process of labrum rounded-truncate; dorsulum shining, first abdominal tergum impunctate ..... *bipunctata* Cress.
Greater part of clypeus punctate or roughened, at most with a median impunctate space 19
19. Second abdominal tergum impressed posteriorly about one-half its length; first tergum finely but distinctly and rather closely punctate; clypeus with a narrow shining impunctate space, remainder strongly and regularly punctate; first recurrent vein not received beyond middle of second submarginal cell ..... *wheeleri* Graen.
Second tergum impressed distinctly less than one-half its length; first recurrent vein received beyond middle of second submarginal cell 20
20. Clypeus coarsely and regularly punctate, strongly roughened between punctures, with a very narrow indistinct median space; mesopleura densely clothed with long gray hair; process of clypeus long, finger-shaped ..... *placida* Sm.
Process of clypeus broad, truncate 21
21. Process of clypeus rounded truncate; facial foveae not distinctly widened toward vertex; clypeus very sparsely and irregularly punctate with a wide impunctate space, slightly roughened and dull; first abdominal tergum shining, finely punctate; terga broadly testaceous at apex, remainder often reddish; stigma and veins light brown to yellow ..... *robertsoni* D.T.
Process of clypeus squarely truncate; facial foveae distinctly widened above; clypeus polished; first tergum sparsely and obscurely punctate, roughened between punctures; terga narrowly testaceous at apex; stigma and veins dark brown 22
22. Clypeus produced, scutellum with two large polished areas, separated by a narrow line of punctures, these areas very sparsely punctate; hairs of tibial scopa rather short ..... *carolina* Vier.
Clypeus not produced; scutellum usually roughened all over, or at least finely tessellate; hairs of scopa rather long, golden brown; terga with apical fasciae of gray, sub-erect hairs; first and second usually clothed with long hairs, others with short sparse pubescence; clypeus strongly and regularly punctate except for a narrow median space, somewhat T-shaped; mesonotum with punctures rather distinct, spaces between punctures tessellate ..... *thaspii* Graen.
23. Apical part of second tergum impressed distinctly less than half of its length 24
Apical part of second tergum impressed half or more than half of its length 25
24. Terga with usually complete apical fasciae; clypeus very closely and regularly punctate, pubescence mostly light gray ..... *kalmiae* n.sp.
Terga without distinct apical fasciae, at most a sparse fringe of hairs; clypeus coarsely and rather sparsely punctate; pubescence mostly dull fulvous ..... *crataegi* Robt.
25. Hind tibiae and tarsi stramineous to reddish; second tergum impressed about one-half; segments usually with partial fasciae of creamy appressed hairs at sides; punctures on clypeus very close and regular ..... *miranda* Sm.
Hind tibiae and tarsi black or brownish; clypeal punctures somewhat irregular 26
26. Second tergum impressed three-quarters or more of its length 27
Second tergum impressed distinctly less than three-quarters of its length 28
27. Space between fovea and margin of eye distinctly wider than fovea at level of antennae ..... *rugosa* Robt.
Space between fovea and margin of eye not as wide as fovea at level of antennae ..... *grandior* Ckll.
28. Space between fovea and margin of eye wider than fovea at level of antennae; abdomen usually with incomplete apical fasciae ..... *ceanothi* Vier.
Space between fovea and margin of eye distinctly narrower than lower part of fovea 29
29. Second tergum impressed one-half distance from base to apex; terga usually fasciate ..... *forbesi* Robt.
Second tergum impressed slightly more than one-half distance from base to apex ..... *mariae* var. *concolor* Robt.

Males

1. Facial line longer than transfacial line; clypeus shining, strongly but sparsely punctate, with an irregular yellow mark; pubescence of body light ..... *bradleyi* Vier.
Facial line shorter than, or at most equal to, transfacial line 2
2. Cheek bordered posteriorly by a distinct keel or ridge, extending up toward the posterior part of eye 7
Cheek rounded or toothed, but not keeled 3

3. Cheek with a prominent tooth or projection on its posterior margin; no black hairs on head 4
   Cheek rounded, without a prominent tooth, at most with a rounded angle 11
4. Mandibles with a prominent tooth near base on lower side 5
   Mandibles without a tooth near base on lower side 6
5. Face and cheeks with long erect hairs, some dark brown, remainder rufous; thorax and first abdominal tergum with long erect reddish hairs; some dark hairs on other terga ..... *milwaukeensis* Graen.
   Face and cheeks with shorter hairs; pubescence of first tergum paler, ochreous to whitish ..... *mandibularis* Robt.
6. Clypeus slightly produced; process of eighth sternum without a shoulder, narrowed behind apex, then widened again to basal plate ..... *carolina* Vier.
   Clypeus not produced, head broad; process of eighth sternum with a shoulder, abruptly narrowed from it to apex ..... *thaspii* Graen.
7. Third joint of antennae at least twice as long as fourth; keel on cheek very prominent; area of cheek between it and eye subquadrate; pleura with a slight rounded projection, less marked than in female of same species ..... *persimulata* Vier.
   Third joint less than twice as long as fourth 8
8. Abdominal terga with more or less complete apical fasciae of appressed pubescence; head broad; area between margin of eye and keel much wider than eye in lateral view 9
   Terga with at most a very thin band of sparse sub-erect hairs; clypeus slightly produced; area between eye and keel scarcely wider than eye ..... *carolina* Vier.
9. Fore wings clouded at apex ..... *nubecula* Sm.
   Fore wings not so clouded 10
10. Apical fasciae closely appressed, remainder of tergum practically bare; mesonotum and scutellum shining; posterior edges of terga broadly testaceous ..... *canadensis* D.T.
    Mesonotum and scutellum somewhat dull; apical fasciae of long, sub-erect, ochreous hairs; remainder of terga more sparsely covered with similar hairs ..... *hirticincta* Prov.
11. Dorsal space of propodeum rugose, bounded posteriorly by a distinct transverse ridge, giving it a truncate appearance; terga with clean-cut punctures, shining between 24
    Dorsal space of propodeum rugulose, granulose, or nearly smooth, not truncate but produced on to posterior face of propodeum and ending in a sharp point, thus forming a triangular enclosure; terga usually roughened, finely, sparsely or not at all punctate (except *A. wilkella*) 12
12. Clypeus yellow 13
    Clypeus without yellow marks 14
13. Cheek only slightly wider than eye in lateral view; abdomen finely and closely punctate; posterior margins of terga broadly testaceous; legs and abdomen usually dull reddish ..... *robertsonii* D.T.
    Cheek nearly twice as wide as eye in lateral view; abdomen tessellate, very sparsely punctate; posterior margins of terga narrowly testaceous; abdomen black; legs black to dull reddish brown ..... *bipunctata* Cress.
14. Face or cheeks with some black or dark brown hairs 15
    Face and cheeks without dark hairs 18
15. Clypeus with pubescence mostly black, closely and strongly punctate; process of labrum sharply truncate; antennal joints three and four sub-equal; process of eighth sternum evenly rounded at apex ..... *algida* Sm.
    Clypeus with pubescence mostly pale; apex of eighth sternal process truncate or slightly notched 16
16. Antennal joint three nearly twice as long as four; sides of propodeum with a large tuft of long black hair ..... *frigida* Sm.
    Antennal joint three distinctly less than twice as long as four; sides of propodeum with pale hair only 17
17. Cheeks and angle between clypeus and eye with a predominance of black hair; joint three of antenna at most equal to joint four; process of eighth sternum with a dorsal and a ventral projection near apex ..... *carlini* Ckll.
    Black hairs of head short and confined to a narrow strip between antenna and eye; joint three of antenna longer than four; process of eighth sternum simple ..... *regularis* Mall.
18. Joint three of antenna almost twice as long as four; antennae reddish brown beneath; posterior borders of terga broadly testaceous; terga shining 19
    Joint three of antenna not conspicuously longer than four, sometimes shorter 20

19. Abdomen long, narrow, slightly reddish; process of eighth sternum long, narrow, tapering, almost acute at apex ..... *salictaria* Robt.
Abdomen rather broad; process of eighth sternum slightly widened toward apex, tip rounded; a slight ventral process or geniculation about two-thirds of distance from basal plate to apex ..... *placida* Sm.

20. Larger, species 10 mm. or more in length; face and thorax normally covered with long, dense, erect ochreous hair; abdomen distinctly but finely punctate 22
Smaller, length 8 mm. or less; face and thorax normally covered with rather sparse whitish or slightly yellowish hair, thickest on clypeus; abdomen roughened, punctures very fine, nearly obscured by roughening 21

21. Clypeus with large shallow punctures, partly obscured by roughening between them; enclosure of propodeum strongly rugulose at base; process of eighth sternum widened at apex, pilosity on ventral surface of process extending back to basal plate; no ventral production or geniculation, first abdominal tergum distinctly punctate ..... *wheeleri* Graen.
Clypeus with deep large punctures, shining between; enclosure of propodeum finely granular at base; process of eighth sternum with a prominent ventral geniculation, pilosity of process not extending more than half distance from apex to basal plate; abdomen usually with a slight greenish reflection ..... *lata* Vier.

22. Abdomen strongly and closely punctate, dull between punctures, with definite apical fasciae, usually complete on segments three and four ..... *wilkella* (Kby.) Ill.
Abdomen finely punctate, shining, no apical fasciae present 23

23. Antennal joint three usually shorter than four; process of eighth sternum with its sides nearly parallel for the apical third when viewed from above ..... *vicina* Sm.
Antennal joint three equal to or longer than four; process of eighth sternum tapering toward apex from basal plate ..... *regularis* Mall.

24. Lateral angles of sixth abdominal sternum reflexed ..... *crataegi* Robt.
Lateral angles of sixth abdominal sternum not reflexed 25

25. Antennae smooth and shining, joint three one-half as long as joint four; abdomen with incomplete apical fasciae ..... *forbesi* Robt.
Antennae dull, joint three more than one-half as long as joint four 26

26. Posterior tarsi and usually tibiae bright reddish testaceous; abdomen with distinct but interrupted apical fasciae 27
Posterior tibiae blackish or brown, tarsi dull brownish 29

27. Rugae of enclosed dorsal space of propodeum nearly straight; process of eighth sternum narrow, apex rounded ..... *miranda* Sm.
Rugae of enclosed space coarse and irregular; process of eighth sternum truncate or slightly notched at apex 28

28. Fourth antennal joint nearly twice as long as third; process of eighth sternum abruptly constricted about two-thirds of the distance from basal plate to apex, then gradually widened toward apex; apex rounded truncate ..... *ceanothi* Vier.
Fourth antennal joint only slightly longer than third, process of eighth sternum without a constriction in its process, abruptly widened at apex; apex slightly notched or bilobed ..... *grandior* Ckll.

29. Dorsal space of propodeum coarsely rugose; clypeus evenly and closely punctate 30
Dorsal space of propodeum less strongly rugose; clypeus with a narrow and indistinct impunctate median space ..... *mariae* var. *concolor* Robt.

30. Dorsal space sharply separated from remainder of propodeum, very narrow at posterior edge; clypeus slightly produced; abdominal fasciae distinct, interrupted on some segments; pubescence of thorax pale ochreous ..... *rugosa* Robt.
Dorsal space very irregularly rugose, almost reticulate, broad at posterior edge, scarcely separated from remainder of propodeum, which is strongly wrinkled; clypeus short and broad; abdomen with fasciae indistinct or wanting; pubescence white or nearly so ..... *kalmiae* n.sp.

A. kalmiae n.sp.

Female

Black; head rather broad; clypeus closely and regularly punctate, with short, sparse, gray or slightly yellowish pubescence; process of labrum truncate or slightly emarginate, shining, much narrower at apex than at base; mandibles reddish brown almost to base, broad at tips, not crossing when closed; antennæ short, light brownish beneath, darker on top, joint 3 about

equal to 4 + 5; facial foveae broad, extending below antennal line, pubescence short, light brownish gray; cheeks shining, finely punctate, with light, sparse, appressed pubescence, longer near base of mandible, rounded, and not much wider than eye in lateral view.

Mesonotum closely punctate at sides, more sparsely so toward centre, tessellate between punctures, pubescence short, sparse, slightly brownish; pleurae rough, somewhat densely clothed with gray hair; scutellum coarsely and sparsely punctate except at posterior border where punctures are close; polished between punctures; metanotum rough, clothed with long hairs; enclosure of propodeum irregularly and closely rugose, truncate posteriorly; surrounding area also roughly rugulose or reticulate, lateral fringe light brownish; wings light brownish, veins and stigma dark testaceous, second submarginal cell narrow, receiving first recurrent vein beyond middle; legs dark brown at base, becoming reddish brown distally, tarsi yellowish, scopa golden yellow, flocculus lighter.

Abdomen shining, terga with narrow brownish posterior borders, distinctly and closely punctate, shining between punctures; pubescence light, short, apical fasciae usually complete on second, third, and fourth terga, but neither dense nor closely appressed, grayish in color; second tergum impressed less than one-third of its length; anal fimbria light brown. Length, 10-11 mm.

Male

Black; head broad; clypeus strongly and very closely punctate, sparsely pubescent; process of labrum broad, slightly emarginate; mandibles stout, reddish at tip; antennae rather stout, brownish, lighter toward tip, third and fifth joints subequal, fourth slightly shorter; cheeks rounded, slightly wider than eye, shining, finely punctate, hairs sparse, grayish.

Mesonotum, not very closely punctate, pubescence short, sparse except at sides, grayish; scutellum shining, with large sparse punctures; metanotum rough; pleura sparsely pubescent, coarsely wrinkled; propodeum much like female, hairs lighter; wings slightly darker than female, stigma reddish; legs dark, tarsi reddish testaceous, pubescence short, pale, yellowish on tarsi.

Abdomen comparatively short and broad, shining, terga often with light brownish borders, distinctly and somewhat closely punctate; hairs sparse, fasciae incomplete, or absent on some segments; second tergum impressed about one-third of its length; sterna with distinct apical fringes of rather long hairs; process of eighth sternum short, wide, abruptly widened at apex. Length 8-9 mm.

This species is very close to *A. daeckei* Vier., especially in the female characters. Miss Sandhouse has kindly compared the females of these species for the writer and has noted the following distinguishing characters: "Punctures of mesonotum finer and more widely separated in *kalmiae;* carinae on enclosure of propodeum in *daeckei* nearly longitudinal instead of irregular in direction; sides of propodeum below the row of long curled hairs shining, almost devoid of punctures or hairs; abdominal tergites with the punctures

of the impressed part more evident in *kalmiae*, hair bands distinctly wider, abdominal terga of *daeckei* appear duller and browner; anal fimbria of *daeckei* pale, hardly yellowish, antennal joint 3 equals one and a half times 4 and 5." The writer has examined the male of *daeckei* and finds that it is smaller; inclining to brownish on abdomen; pubescence of a yellowish tinge; antennae light brown, propodeum with nearly longitudinal rugae much more regular than in *kalmiae;* veins and stigma dark ferruginous; process of eighth sternum rather slender, not conspicuously dilated at apex.

Types. Male and female, Kings County, Nova Scotia, Canada, July 9, 1931, on *Kalmia angustifolia* L.

Paratypes. One additional male of same date, two more July 13, 1932; 14 females June 24, 1931; 3 females July 9, 1931; 6 females July 13, 1932, collected by C. E. Atwood; one male and 5 females July 9, 1931, collected by Dr. W. H. Brittain; all on *Kalmia* and from Kings County, N.S. Types in the National Collection, Ottawa. Other specimens exchanged not in type series, including one male taken on *Ledum*, Kings County, June 24, 1932.

A. ceanothi Vier.

A. ceanothi Viereck, Trans. Am. Ent. Soc. 43 : 404; 1917.

Female

Black; clypeus shining, coarsely punctate, with punctures more numerous toward sides and base, very sparse toward apex, hairs dull fulvous; process of labrum squarely truncate; mandibles red at base; antennae black, joint 3 longer than 4 but not equal to 4 + 5; facial foveae broad above, abruptly narrowed from just above antennae to a narrow furrow with some long hairs in it as well as the usual appressed pubescence, and separated from eye margin by a space about equal to this narrowed part of fovea in width; cheeks rounded, narrow, finely and somewhat closely punctate, with pale fulvous hairs.

Mesonotum and scutellum coarsely punctate, punctures often adjoining along margins, with short, erect, fulvous pubescence; pleura very rough, with longer and paler hairs; enclosure of propodeum short, truncate behind, rugose, with about 20 distinct rugae, short at sides; sides of propodeum with pale fulvous hairs, rather long, surface strongly, irregularly rugose; wings faintly tinged with brown, veins and stigma dark brown, tegulae ferruginous; legs black or dark brown, tarsi reddish, flocculus ochreous, scopa and pubescence of legs in general pale fulvous.

Abdomen shining, densely punctate, second tergum impressed about two-thirds of its length, dense fasciae of whitish or rich creamy hairs on apical margins of terga, sparse fulvous hairs on basal parts of terga; anal fimbria reddish brown. Length 9-10 mm.

Male

Black; clypeus densely pubescent, closely and strongly punctate, with a suggestion of narrow median impunctate space, punctures often confluent;

process of labrum truncate; mandibles reddish at tip, black at base, apex bluntly rounded; antennae black or slightly brownish, rather stout, fourth joint almost twice as long as third and about equal to fifth; cheeks rounded, densely pubescent.

Mesonotum coarsely and regularly, not very closely punctate, tessellate between punctures, covered with erect hairs somewhat more dull than those of head; scutellum more coarsely and sparsely punctate, shining anteriorly; metanotum dull, strongly roughened, with obscure punctures; pleura densely pubescent, very closely punctate; enclosure of propodeum distinct, rather long, coarsely rugose; sides of propodeum coarsely wrinkled or reticulate, densely pubescent; wings brownish, veins dark testaceous or brown, stigma reddish; first recurrent vein received beyond middle of second submarginal cell; tegulae dark testaceous; legs dark reddish-brown near base, tarsi and posterior tibiae reddish stramineous, the latter with a dark spot, other tibiae sometimes partly yellowish; pubescence short, light.

Abdomen black, shining, terga with brownish apices, second tergum faintly impressed about one-third of its length; first and second terga finely but distinctly punctate, others more obscurely so; hairs very short and sparse, incomplete apical fasciae at sides; anal fimbria pale yellowish; process of eighth sternum sharply constricted near apex, then abruptly widened again at tip; basal plate of sternum very wide. Length about 8 mm.

The male which Viereck has described under this name is incorrectly associated with the female. The male described above was taken *in copula* with a female which agrees with Viereck's type. Viereck's male (paratype) differs from the above in the following details: clypeus with finer punctures, more sparse toward centre; pubescence shorter and more sparse; mandibles broad, pre-apical tooth small; antennae very slender, especially at base, brownish or reddish; scutellum and metanotum more closely punctate, shining; propodeum with short sparse hairs; tarsi ferruginous; abdomen slender, first tergum almost impunctate, highly polished; eighth sternum without a constriction near apex of process, but gradually widening from near middle of process to a rounded apex.

This will leave Viereck's male without a name but it is better not to propose a new one until someone has had an opportunity of associating it with the proper female, which, of course, may be already named.

Male, *in copula* with typical female, Kings County, Nova Scotia, Canada, May 18, 1931, on the cultivated plum (*Prunus*); 9 other males and 11 females, Kings, Digby, and Lunenburg counties (May 8 to July 3). Rather common on apple and plum.

The Genital Armature of *Andrena* and *Halictus*

The following drawings are an attempt to show some of the characters of the eighth and ninth abdominal sterna of males of the two genera under consideration. The writer's attention was drawn to these structures by a paper by Morice (4). The characters appear to be constant and of consider-

able taxonomic value, especially among the species related to *A. rugosa* Rob., where the males are much alike externally. Among the *Halicti* the characters are not so satisfactory but are still of value.

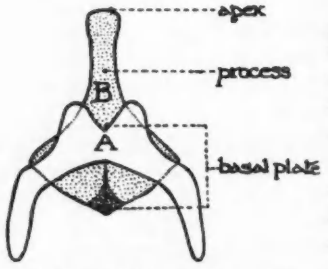

FIG 1. *Eighth ventral segment.*

Morice was somewhat mistaken in his interpretation of the structures which he illustrated. He considered that the "ventral valve (valvula ventralis)" was the eighth sternum, neglecting the "transferred segment" (propodeum), which would make the "ventral valve" the true ninth sternum, and the "stipes", bearing the various clasping organs, the tenth, whereas it is well known that the parameres of insects are found on the true ninth sternum. An examination of the ventral segments of *Andrena* will show a condition somewhat like that given by Fig. 1, which shows the eighth sternum in ventral view.

Eighth sternum of Andrena

The true eighth sternum is secondarily divided and the posterior and dorsal part, stippled and labelled "B" in the diagram, forms the "ventral valve". The anterior and ventral part of the eighth sternum has a posterior notch, into which the process of the "ventral valve" fits. This portion of the segment has been neglected in the drawings which follow.

The condition which obtains in the true ninth segment (Morice's "stipites") is shown in Fig. 2, which gives a dorsal view.

Ninth sternum of Andrena

The outer claspers have a common base, a dorsal "lobe", and a posterior and somewhat ventral "process", and enclose a second pair of claspers, which are the parameres. The aedeagus lies below these and is not visible in the dorsal view. The base and the parameres are neglected in the drawings.

The condition in *Halictus* is quite similar, but the eighth sternum is less apparently divided, and the processes of the stipites have other processes and brushes posteriorly and ventrally.

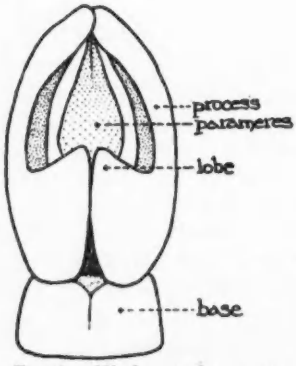

FIG. 2. *Ninth ventral segment.*

The drawings were made from mounts prepared by boiling the parts in potash solution and then mounting them. The structures of the *Andrenae* and the stipites of the *Halicti* were mounted in glycerine and small supports put under the cover glass to prevent crushing; the eighth sterna of the *Halicti* were stained and mounted in balsam. In general, the ventral view of the

eighth and the dorsal view of the ninth sterna are given, but in some cases dorsal or lateral views of the apices of the eighth sternal processes are also shown.

Acknowledgments

It is with great pleasure that the author takes this opportunity of expressing his thanks to those who have helped in the preparation of the paper by supervision of work, determination of species and loans of material.

The laboratory study of the species concerned has been done largely in the Department of Biology, University of Toronto; the field work was carried on while the writer was in the employment of the Entomological Branch, Department of Agriculture, Ottawa. Dr. E. M. Walker directed the later taxonomic work and his guidance on morphological points, the construction of keys and the preparation of drawings is gratefully acknowledged. The collection of material, preliminary classification and biological studies were carried on under the guidance of Dr. W. H. Brittain of Macdonald College, McGill University, whose experience in entomological matters has been of the greatest assistance in this work. Through the good offices of Dr. B. A. Bensley, Head of the Department of Biology at Toronto, and the courtesy of Dr. Harold Morrison, of the U. S. Bureau of Entomology, the author was enabled to spend some time in the National Museum at Washington, D. C., an opportunity which aided greatly in the identification of material. Miss Grace Sandhouse of the Bureau has aided in many ways, especially by identifying material and establishing synonymy of species. Finally, very many thanks are due to the members of the Entomological Branch, Mr. Arthur Gibson and his staff, to the staffs of the Royal Ontario Museum of Zoology, the Ontario Agricultural College, and the Nova Scotia Agricultural College, as well as to Mr. A. F. Winn of the Redpath Museum, McGill University and Mr. Buckle of Montreal for encouragement, advice and the loan of specimens and literature.

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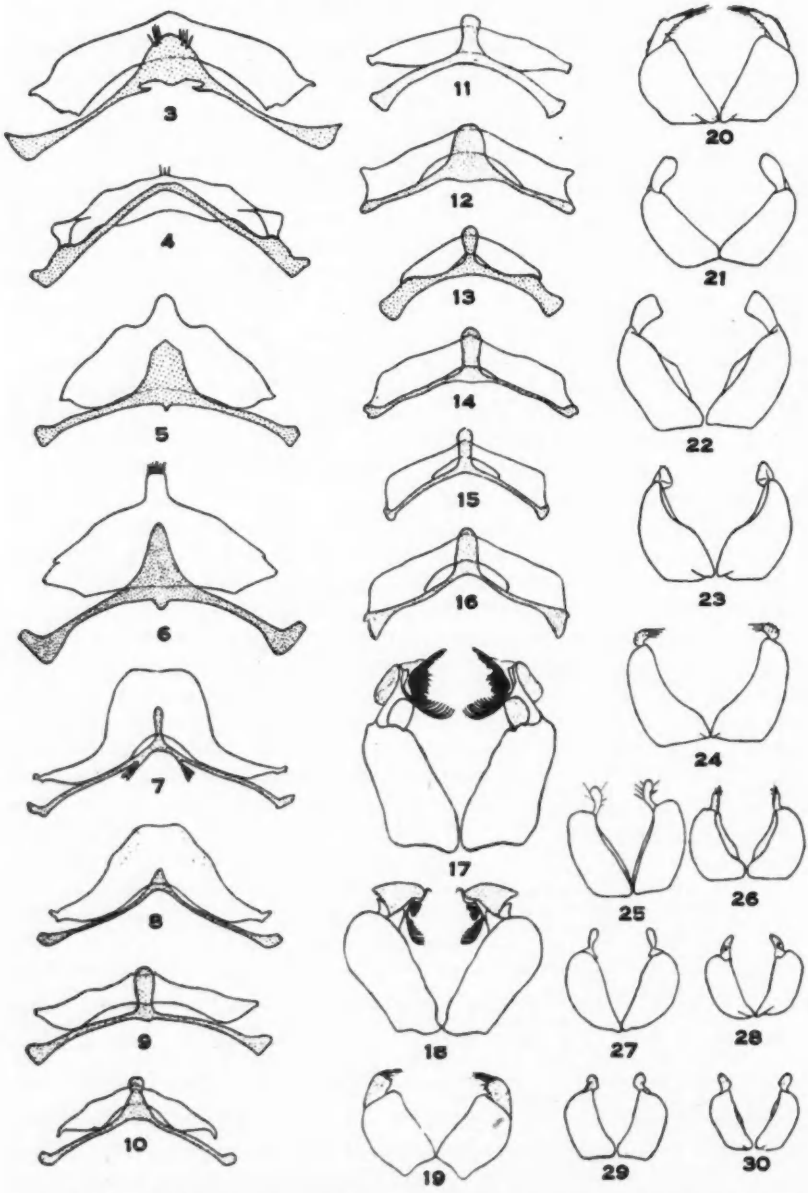
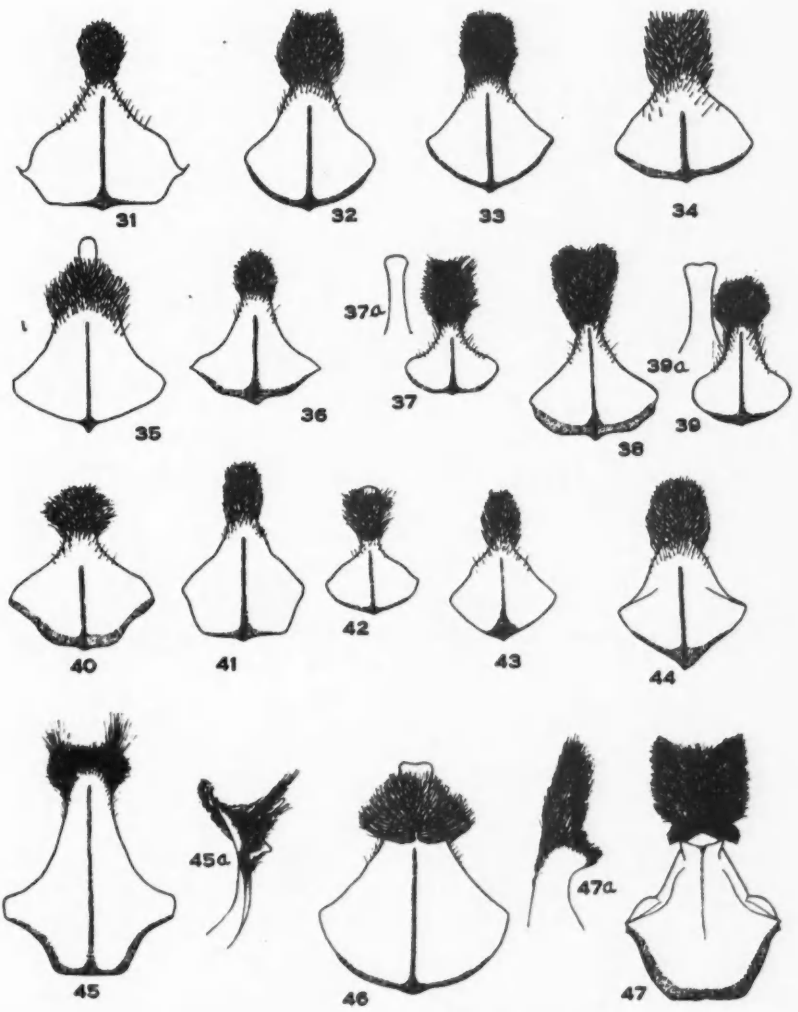
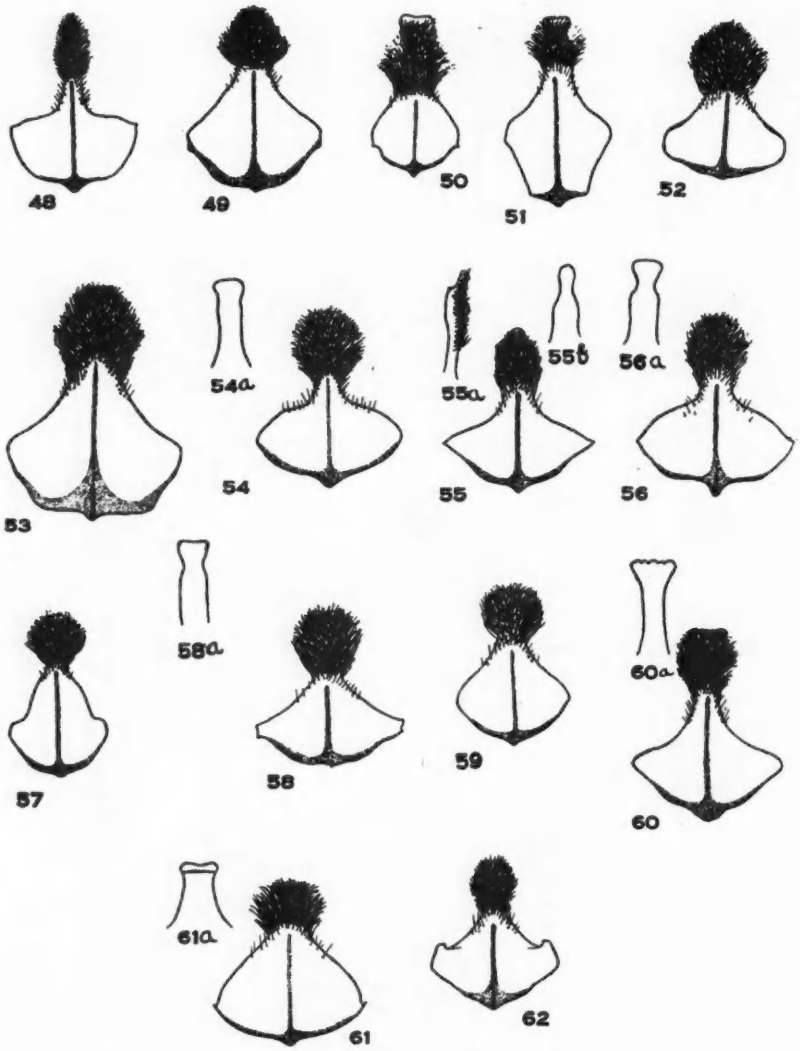


FIGS. 3–16. *Eighth ventral segments of male Halictus spp.* (×23) 3. *Halictus rubicundus (Christ.) Kby.* 4. *H. provancheri D.T.* 5. *H. athabascensis Sandh.* 6. *H. coriaceus Sm.* 7. *H. zonulus Sm.* 8. *H. leucozonius (Schrank) LeP.* 9. *H. arcuatus Rob.* 10. *H. pectoralis Sm.* 11. *H. rufitarsus Zett.* 12. *H. consonus Sandh.* 13. *H. foxii Rob.* 14. *H. viridatus Lov.* 15. *H. pilosus Sm.* 16. *H. nymphaearum Rob.*

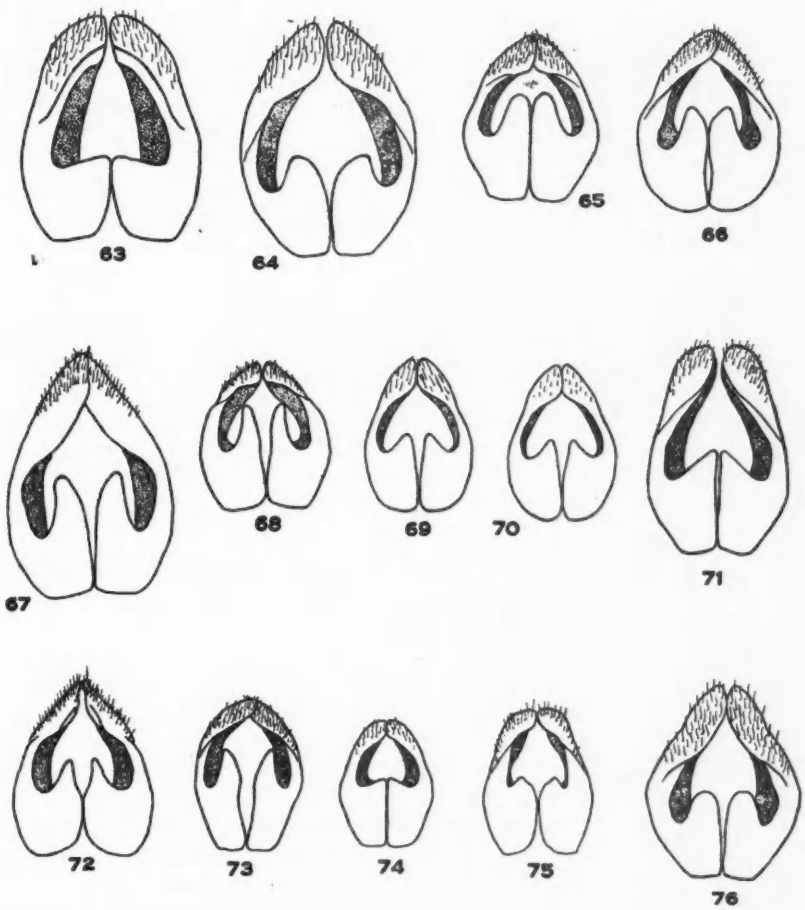
FIGS. 17–30. *Stipites of male Halictus spp.* (×23). 17. *Halictus rubicundus (Christ.) Kby.* 18. *H. provancheri D.T.* 19. *H. athabascensis Sandh.* 20. *H. coriaceus Sm.* 21. *H. zonulus Sm.* 22. *H. leucozonius (Schrank.) LeP.* 23. *H. arcuatus Rob.* 24. *H. consonus Sandh.* 25. *H. rufitarsus Zett.* 26. *H. pectoralis Sm.* 27. *H. nymphaearum Rob.* 28. *H. pilosus Sm.* 29. *H. viridatus Lov.* 30. *H. foxii Rob.*



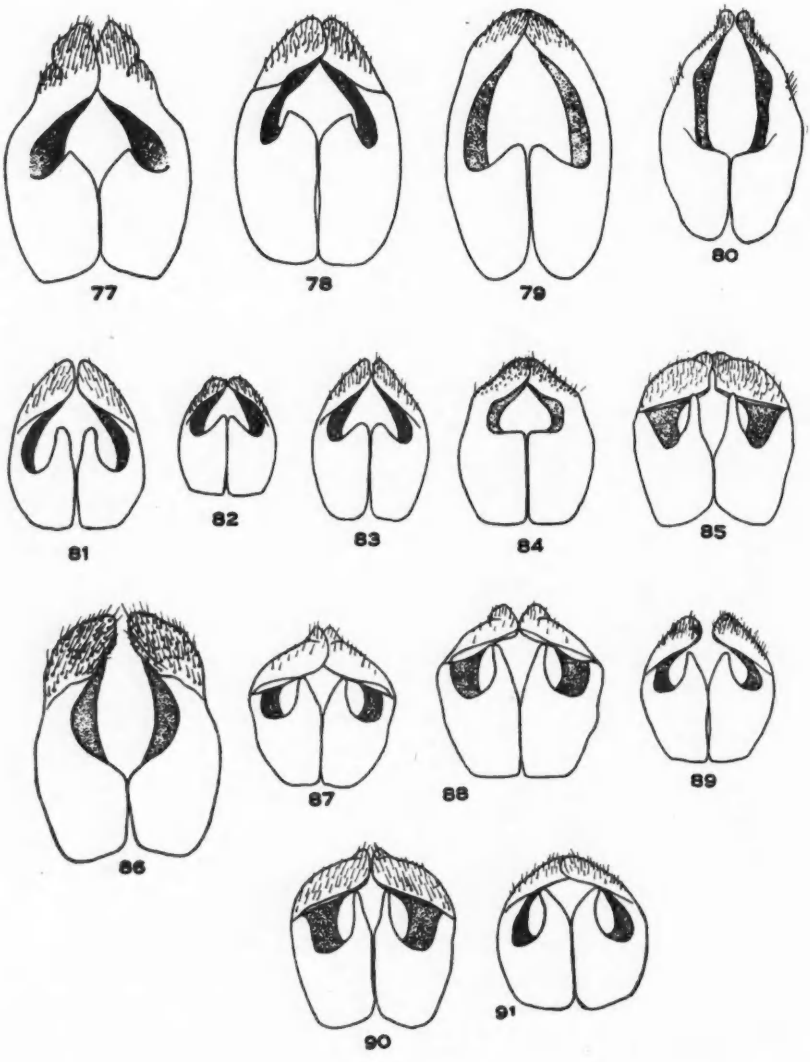
FIGS. 31–47a. *Part of eighth ventral segment of male Andrena spp.* (×23). 31. *Andrena bradleyi Vier.* 32. *A. milwaukeensis Graen.* 33. *A. mandibularis Rob.* 34. *A. carolina Vier.* 35. *A. thaspii Graen.* 36. *A. persimulata Vier.* 37. *A. nubecula Sm.* 37a. *A. nubecula (dorsal).* 38. *A. hirticincta Prov.* 39. *A. canadensis D.T.* 39a. *A. canadensis (dorsal).* 40. *A. robertsonii D.T.* 41. *A. bipunctata Cress.* 42. *A. algida Sm.* 43. *A. vagans Ckll.* 44. *A. frigida Sm.* 45. *A. carlini Ckll.* 45a. *A. carlini (lateral).* 46. *A. regularis Mall.* 47. *A. vicina Sm.* 47a. *A. vicina (lateral).*



FIGS. 48–62. *Part of eighth ventral segment of male Andrena spp. (cont'd.)* (× 23). 48. *Andrena salictaria Rob.* 49. *A. placida Sm.* 50. *A. wheeleri Graen.* 51. *A. lata Vier.* 52. *A. wilkella (Kby.) Ill.* 53. *A. crataegi Rob.* 54. *A. forbesi Rob.* 54a. *A. forbesi (dorsal).* 55. *A. miranda Sm.* 55a. *A. miranda (dorsal).* 55b. *A. miranda (lateral).* 56. *A. ceanothi Vier.* 56a. *A. ceanothi (dorsal).* 57. *A. sp. (incorrectly described by Viereck as the male of ceanothi).* 58. *A. rugosa Rob.* 58a. *A. rugosa (dorsal).* 59. *A. grandior Ckll.* 60. *A. mariae var. concolor Rob. (?).* 60a. *A. mariae var. concolor Rob. (?) (ventral).* 61. *A. kalmiae n.sp.* 61a. *A. kalmiae (dorsal).* 62. *A. daeckei Vier.*



FIGS. 63–76. *Stipites of male Andrena spp.* (× 23). 63. *Andrena bradleyi Vier.* 64. *A. milwaukeensis Graen.* 65. *A. mandibularis Rob.* 66. *A. carolina Vier.* 67. *A. thaspii Graen.* 68. *A. persimulata Vier.* 69. *A. nubecula Sm.* 70. *A. canadensis D.T.* 71. *A. hirticincta Prov.* 72. *A. robertsonii D.T.* 73. *A. bipunctata Cress.* 74. *A. algida Sm.* 75. *A. vagans Ckll.* 76. *A. frigida Sm.*



FIGS. 77–91. *Stipites of male Andrena spp.* (× 23). 77. *Andrena carlini Ckll.* 78. *A. regularis Mall.* 79. *A. vicina Sm.* 80. *A. salictaria Rob.* 81. *A. placida Sm.* 82. *A. wheeleri Graen.* 83. *A. lata Vier.* 84. *A. wilkella (Kby.) Ill.* 85. *A. forbesi Rob.* 86. *A. crataegi Rob.* 87. *A. miranda Sm.* 88. *A. ceanothi Vier.* 89. *A. grandior Ckll.* 90. *A. mariae var. concolor Rob.* (?). 91. *A. kalmiae n.sp.*

EXPERIMENTAL DRYING EQUIPMENT FOR ALIMENTARY PASTES[1]

By D. S. Binnington[2] and W. F. Geddes[3]

Abstract

An apparatus is described whereby the experimental drying of alimentary pastes may be conducted automatically under a pre-determined program of temperature, time and humidity relations.

The air employed for drying is continuously recirculated, dehumidification being obtained by by-passing an increasing proportion over refrigerating coils through the medium of an especially designed valve, operated electromagnetically and timed by an electric clock.

Complete control of the time-humidity relation is obtained by a regulated steam input from a water resistance boiler controlled by the action of the wet bulb recording pen in conjunction with a conducting strip placed on the recorder chart.

While specifically designed for drying alimentary pastes, the apparatus should be well adapted to other classes of drying studies and may also be employed to maintain constant conditions of temperature and humidity.

Introduction

The removal of excess water from various forms of alimentary pastes, such as macaroni and spaghetti, is generally conceded to represent the most critical stage of the entire manufacturing process. If the operation is unduly rapid, surface drying occurs, resulting in cracking, checking and curling, and if too slow, there is danger of chemical and bio-chemical changes, such as souring and molding, taking place.

The critical factor in the drying operation appears to be the rate of diffusion of water from the centre to the outside of the material, and the ideal drying condition, therefore, is one that will remove the surface moisture at a rate that exactly parallels this diffusion. Modern commercial practice approximates this condition by drying under a falling humidity gradient, which is obtained by: *A*, raising the temperature of the air used for the drying process; *B*, allowing a portion of the moisture laden air to vent to the atmosphere, replacing it by air at atmospheric humidity; *C*, a combination of *A* and *B*. The first method, *A*, is subject to the disadvantage of the comparatively high temperatures needed to obtain the desired reduction in humidity. The use of such temperatures is considered by the older school of macaroni makers to be very detrimental to the product. No definite evidence however appears to be available on this point. The chief criticism of methods *B* and *C* is that they are not accurately controllable, owing to variations in atmospheric humidity, and are therefore of doubtful value for experimental studies.

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The testing of durum wheats for quality obviously requires that the entire sequence of operations from the milling of semolina to the drying of the finished product be conducted under carefully controlled and reproducible conditions. This was the principal consideration in the design of the apparatus to be described. However, in view of the fact that so little information is available regarding the effects of varying conditions of time, temperature and rate of humidity fall, on the drying operation, it was deemed advisable to make suitable provision for investigating these different factors.

A preliminary survey indicated that no commercially built apparatus was available that would fulfil the necessary requirements, and that equipment in the few existing small-scale units was not capable of sufficiently accurate control for our purpose. It thus became necessary to design and construct a drying cabinet that would:—

(i) maintain a constant temperature throughout the range from room temperature to 120° F;

(ii) produce and maintain any desired relative humidity up to and including saturation within the entire temperature range, and independent of external humidity;

(iii) incorporate means for producing an automatically falling humidity gradient, and for varying this rate of fall within wide limits, but keeping the temperature constant at any desired value;

(iv) incorporate means for producing an automatically falling humidity gradient by slowly and progressively raising the temperature;

(v) incorporate means for circulating the "conditioned" air in a stream of uniform cross-sectional velocity over the material to be dried, with provision for varying the velocity if necessary;

(vi) provide suitable instruments for indicating and recording temperature and relative humidity.

The apparatus as finally developed operates as follows. Air is forced by a fan through a drying chamber containing the macaroni or spaghetti to be dried. This is suspended in the conventional manner over round wooden sticks which are supported on suitable carriers. The moisture laden air leaving the drying chamber may be divided into two streams by a valve, one passing through a section containing refrigerating coils, the other flowing through a by-pass. The air streams unite, mix, and pass to a chamber containing heating coils thermostatically controlled, before returning to the drying chamber. A closed circuit is thus maintained, the same air being continuously recirculated. By gradually and progressively opening the valve, an increasing proportion of the air is caused to flow over the cooling coils, moisture is frozen out, and a decrease in the relative humidity of the air returning to the cabinet is obtained. Thus, by varying the rate of motion of this valve, any desired humidity gradient may be produced, temperature being kept uniformly constant.

Constructional Details

The general constructional details are fully illustrated in Fig. 1 together with the location of the accessory heating, humidifying and dehumidifying apparatus.

Framework and Cabinet

The framework was built of 3 by 3 in. stock in three sections, afterwards bolted together, using strips of felt between the adjacent faces to act as gaskets. The central section contains the drying chamber proper which is built from 1 by 4 in. tongued and grooved fir. This chamber was constructed in such a manner that the carriers when introduced, occupy the entire cross-sectional area, compelling the air stream to flow through the material being dried. Three rabbeted doors are fitted, equipped with double glass for thermal insulation. These are provided with rubber refrigerator door insulation and standard refrigerator hinges and catches in order to secure a reasonably air-tight fit. The entire interior surface is moisture proofed with two coats of hot raw linseed oil, and three coats of high grade spar varnish. Two small inspection windows, 6 by 8 in., are placed in the top of the drying section. The end sections containing the inlet and outlet cones are completely panelled with three-ply veneer, with the exception of the left end, which is fitted with a slate panel, serving as an instrument board.

Seven galvanized iron louvres, 4 by 23½ in., are fitted at each end of the drying chamber, permanently attached to ¼ in. brass rods passing through the front and back walls of the cabinet. At the rear, a steel bearing plate is provided, attached to the outer wall of the drying chamber. Tension to maintain the louvres in place is obtained with short coil springs, held in place by washers and split pins. The front bearing plate is of brass, and is attached to a removable panel, rabbeted and provided with felt gaskets. The entire louvre assembly may be removed together with this panel by unscrewing and detaching the tension springs at the rear. The forward ends of the brass rods are provided with knurled knobs to which are attached short arms fitted with steel locating pins. These pins may be locked in any one of a number of small holes drilled in the brass plate, by simply pulling the rod forward against the spring tension, rotating to the desired position and releasing. In this way adjustment of the louvres and consequent uniformity of air flow may be secured and maintained without opening the doors of the drying cabinet.

The Fan

This is a "Series 30" Size No. 1, Canadian Sirocco, equipped with a ½ h.p. motor. After being placed in service, difficulty was experienced owing to leakage and venting of air from the apparatus, which was finally traced in part to a constructional feature of this fan. With small sized fans of this type, a special bearing for the rotor is dispensed with, the entire load being carried by the motor bearings. Presumably owing to this fact, a comparatively large opening is made in the side of the fan housing allowing

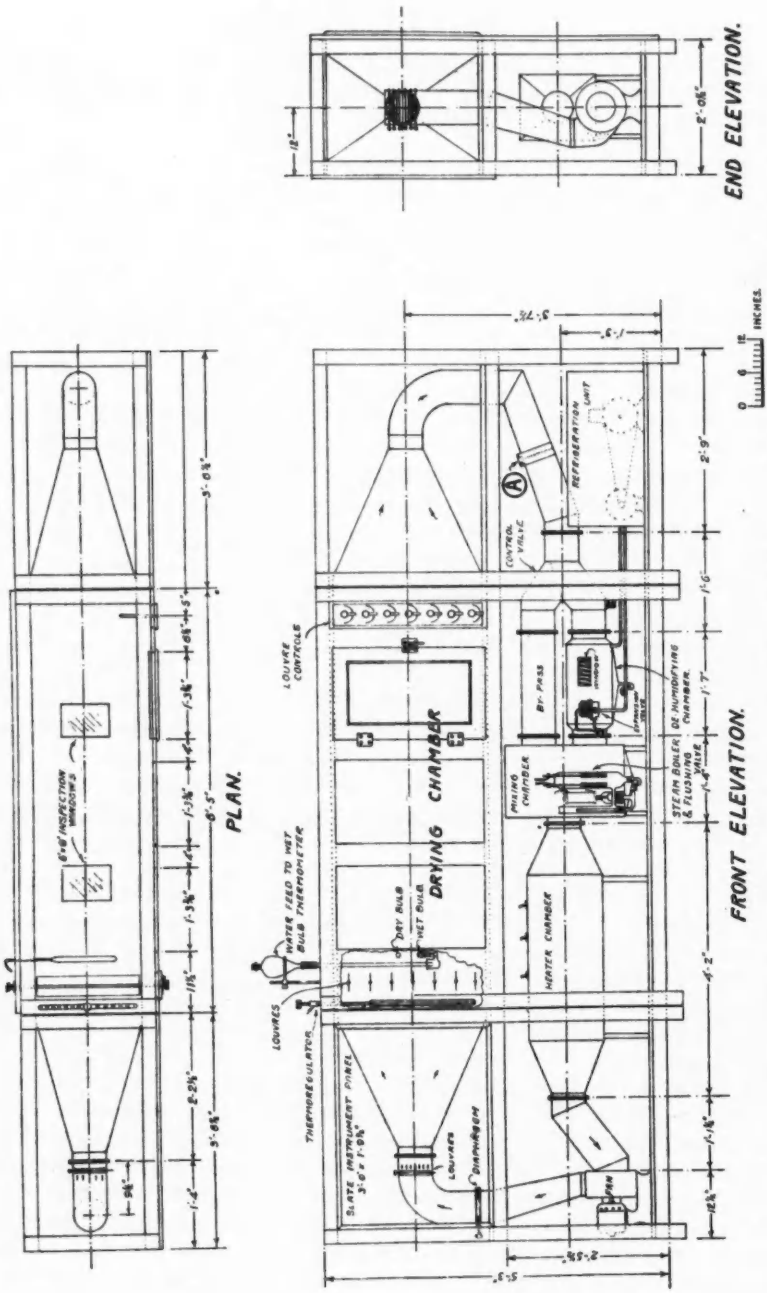

FIG. 1. *General working drawing showing main constructional features and location of accessory apparatus.*

¼ to ⅜ in. clearance around the fan hub. At high speeds, and particularly in a closed circuit, steady leakage takes place through this opening. Heavy felt gaskets were tried in an attempt to seal this opening, but lasted only a short time, and final solution of the difficulty was accomplished only by entirely enclosing the space between the end of the motor casing and the side plate of the fan. This was done by soldering a short sheet metal cylinder directly onto the end of the motor and luting the other end of the cylinder to the fan housing with battery pitch. Suitably closed apertures were provided for oiling the motor bearing, and attaching the fan to the motor shaft. The regular ventilation opening in the end of the motor was closed with a metal plate, and other openings drilled external to the enclosing cylinder. A metal slide accommodating brass diaphragm plates of various apertures is fitted between the fan and the inlet cone, thus making possible control of air velocity without altering the speed of the fan.

Sheet Metal Work

The various chambers and ducts of the apparatus are built from 26 to 28 gauge galvanized iron, 18 gauge being employed for the inlet and outlet cones.

In order to facilitate the assembly of the various parts, brass flanges cast from an especially prepared pattern are employed. These are mated in pairs, provided with locating marks, and soldered to the portions to be connected. Gaskets of $\frac{1}{16}$ in. sheet rubber are used to secure a tight joint. The entire assembly of auxiliary apparatus is made in this manner (working from left to right), with the exception of the final connection, (point "A") Fig. 1. This is made by butting the ends of the air ducts together, surrounding by a clamping band of heavy sheet metal, and sealing the edges with battery pitch. This material is used throughout for sealing minor openings, larger ones being stopped by a plastic mass of paper towelling pulped with a hot rosin soap solution.

Heating System

This consists of suitable elements placed in the air stream, and controlled by a sensitive thermoregulator.

The heating unit is made from 18 B and S gauge Chromel "A" wire threaded back and forth between two sheets of asbestos transite ¼ by 11½ by 29½ in., spaced 10½ in. apart by 6¼ in. brass rods. The wire is introduced in uncoiled lengths of approximately 10 ft. and connected to bolts at each end; 28 of these units are joined in series of seven, giving four heaters of 3.8 amperes capacity each. This method of wiring, though tedious, gives a heating unit of large radiating surface and very low lag.

This heater is housed in a rectangular metal section, 30 by 12 by 12 in. (exclusive of the coned ends), and lined throughout with asbestos paper. The entire heating unit is inserted through the front, which is then closed by a flat metal plate bolted onto flanged edges covered with strips of sheet rubber. The four heaters are connected to individual switches, two being

controlled by a mercury-toluene thermoregulator of the grid type, similar to that described by Wing (2), placed immediately behind the louvres at the inlet end of the drying chamber. An American Instrument Company super-sensitive relay with a maximum capacity in excess of 1000 watts is employed. This relay is mounted on the control panel together with a pilot lamp. The upper (adjustable) contact of the thermoregulator projects through the top of the cabinet, so that final setting of temperature may be accomplished without opening the doors.

Mixing Chamber and Humidifier

The mixing chamber, 12 by 21 by 8 in., contains approximately 30 sq. ft. of 12 mesh bronze gauze, suspended in strips $\frac{1}{4}$ in. apart. Humidification is accomplished by means of a steam generator (Fig. 2), built of Pyrex glass, employing the principle of direct water resistance as a heating medium.

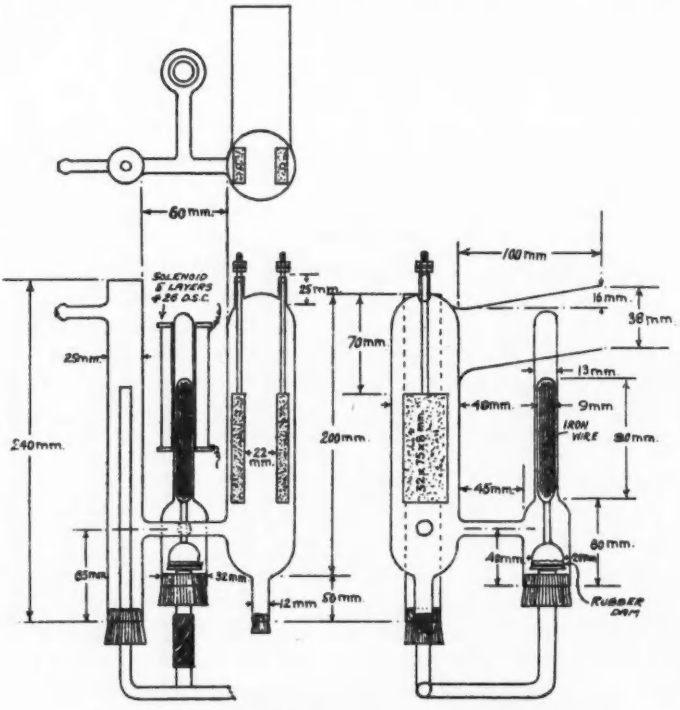

FIG. 2. *Details of steam generator and flushing device.*

Carbon plate electrodes of 3 sq. in. area each, threaded onto brass rods are used, a constant feed serving to supply tap water to the boiler. Owing to the small amount of water contained in the boiling chamber, steam is generated in approximately one minute and ceases the instant that either the water supply is exhausted or the current interrupted.

Continued operation of this type of boiler results in an accumulation of soluble salts which decrease the resistance appreciably. Uniformity of operating characteristics may be secured by draining manually at fairly frequent intervals, but for long runs automatic control is desirable. This is attained by a simple valve actuated by a solenoid, the rate of operation of which is controlled by an electric clock with suitably spaced contacts. A single contact of suitable width on the face, and a brush on the minute hand giving one flush of about 30 to 45 sec. duration per hour, is entirely satisfactory with the water supply available to the writers. The entire assembly of boiler, flushing valve and constant level is constructed from Pyrex glass, as a single unit, and is illustrated in Fig. 2.

The presence of the bronze mesh in the chamber assists in mixing the entering air streams. Baffles are provided over the inlets and exit in this chamber to minimize entrainment of water spray in the air stream.

Dehumidifying Equipment

Dehumidification of the circulating air is accomplished in a chamber containing 90 ft. of $\frac{3}{8}$ in. copper tubing wound in three concentric layers. Liquid sulphur dioxide is supplied to this coil from a $\frac{1}{3}$ h.p. Frigidaire Compressor unit (Model A 233), through a thermostatically controlled expansion valve. The methyl chloride thermostat bulb actuating this control is placed in close contact with the cooling coils. In addition, the valve is equipped with a manual control, which may be adjusted for any desired back pressure or vacuum that experience may dictate, a suitable vacuum and pressure gauge being provided. A trapped drain is placed in the bottom of the refrigerating section to remove condensed water as it accumulates.

Valve and Operating Mechanism

The valve is illustrated in Fig. 3. The body is built up from $\frac{3}{32}$ in. brass plate, the edges being butted together and soft soldered. The valve plate is cut from $\frac{1}{8}$ in. brass, and is attached to its shaft by small machine screws, and balanced by an external counterweight. If sufficient care is exercised in the construction of the casing and the fitting of the valve itself, not more than $\frac{1}{64}$ in. clearance at each side should be necessary for free working. Adjustable stops are provided at each end of the travel in order to prevent the valve from locking. These stops are set to $\frac{1}{32}$ in. opening.

The operating mechanism is shown in detail in Fig. 4. It consists of a ratchet (184 teeth) actuated by an electromagnet. The motion of the ratchet is communicated to the valve by a train of gears (5 to 1 reduction) through the medium of a flexible coupling. When current is supplied to the electromagnet the pawl is pulled forward into the next space of the ratchet. As soon as the current is interrupted, the pawl is returned to its original position by means of a tension spring, thereby causing the ratchet to move through the distance represented by a single tooth (approximately $\frac{1}{16}$ in.). The electromagnet is wound with four layers of 18 B and S gauge bell wire, and

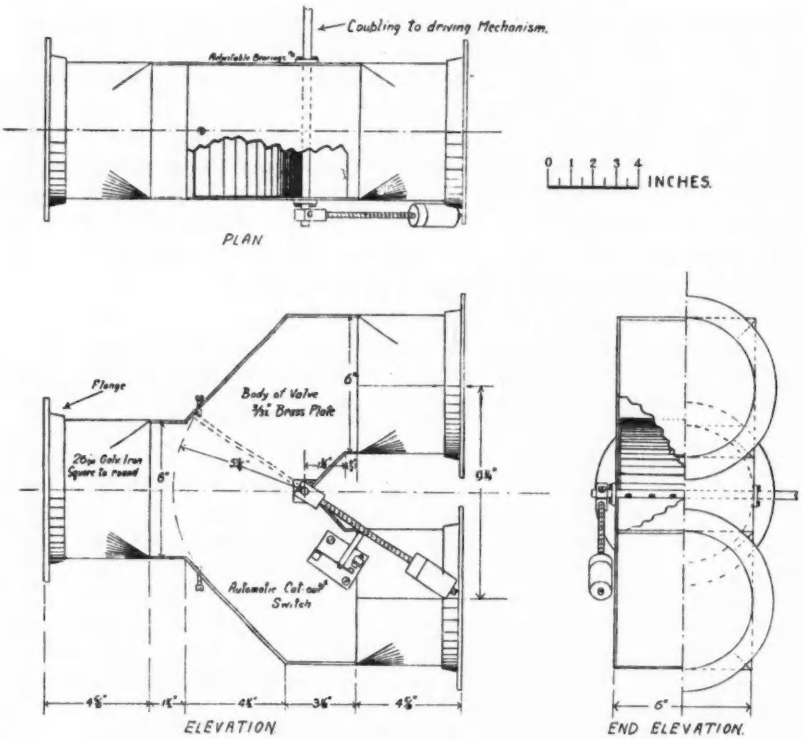

FIG. 3. *Details of by-pass valve.*

operates on a six volt battery at seven amperes. A switch operated by the valve counterweight is provided in order to disconnect the electromagnet when the valve reaches the end of its travel.

The timing of the impulse is obtained with an electric clock. This is provided with 24 narrow brass contacts set flush in an insulating ring of hard rubber, and spaced at 2½ min. intervals. Each contact is wired to an individual switch, the circuit being completed by a very small brush of platinum foil attached to the end of the minute hand. A two-volt current is employed in this circuit to operate a relay, which controls the current to the electromagnet. With every switch in the circuit, the valve thus receiving an impulse every 2½ min., approximately 5 hr. are required to effect complete opening. By cutting out the switches in suitable order the valve may be opened in 5, 10, 20, 30, 40, 60, or 120 hr. In addition, this order may be varied, thus shortening or extending the rate of opening at any desired stage of the drying operation.

Temperature and Humidity Recording Instruments

Changes in temperature and relative humidity are followed by means of a 24-hr. chart two-pen recording thermometer, one bulb of which records air

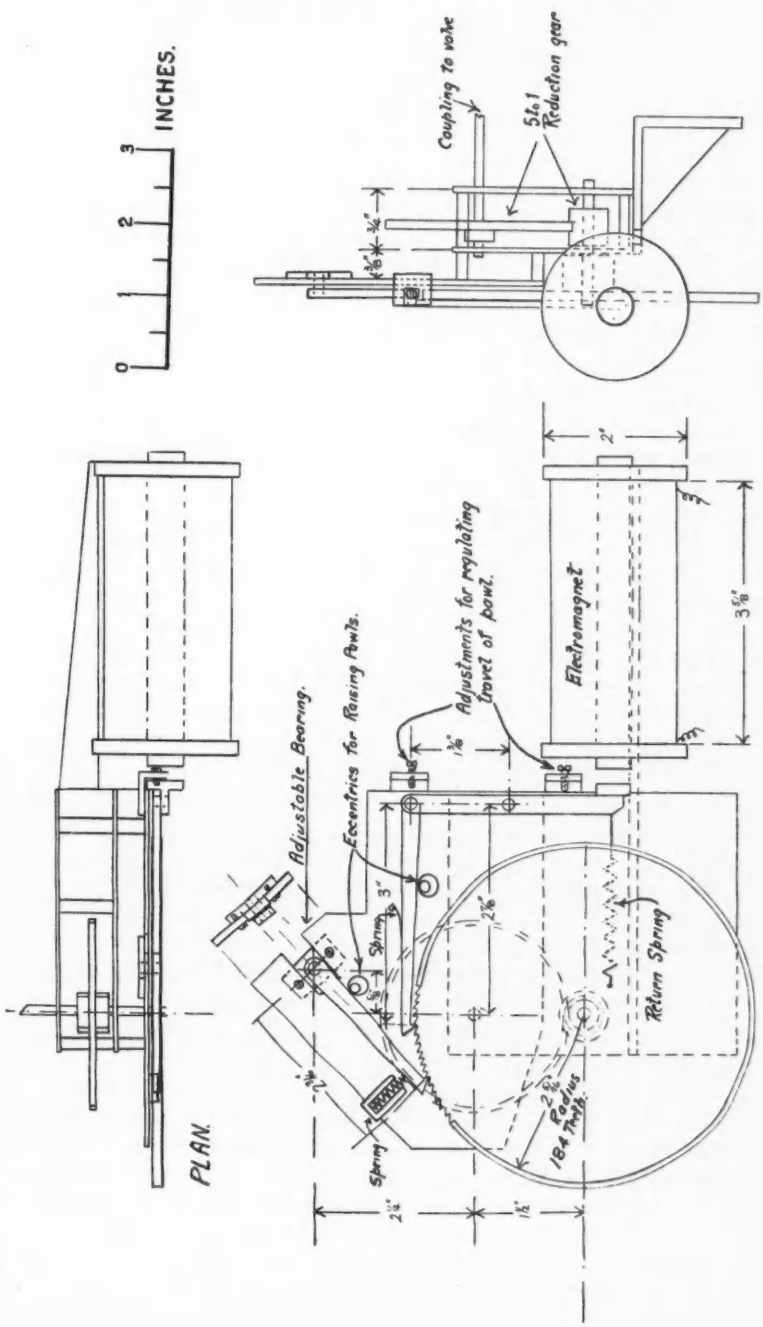

FIG. 4. *Details of valve operating mechanism.*

temperature, and the other, wet bulb temperature. The bulbs are placed at the inlet end of the cabinet, as indicated in Fig. 1. The lower (wet bulb) is wrapped in thin silk and fed with distilled water from four separate wicks dipping into cups attached to a common header crossing the cabinet from side to side, and provided with levelling adjustments at each end.

Wiring and Controls

The controls, switches, recording thermometer, relays and timing clock are located on the slate instrument panel previously mentioned. Wiring is carried to this point in No. 14 B.X. and divided into four circuits individually fused before connecting to the 110-220 volt line. The entire wiring diagram is illustrated in Fig. 5.

Humidity Gradient Control

Initial tests with the apparatus as described showed a rapid drop in relative humidity from saturation to about 82%. This drop is probably due to leakage of air from the system, and may be offset by means of an automatically regulated steam input from the humidifier.

Commercial control instruments are available for the production of predetermined time-temperature and time-humidity gradients. These instruments produce the required gradients by means of metal cams which actuate a compressed air system of valve control. Both fixed and variable cams may be obtained but the degree of adjustment in the latter type is confined to a limited portion of the time range. For experimental work, a large number of cams would be required and it seemed advisable to devise a method of control which would allow of the production of any desired humidity or temperature gradient without recourse to the cutting of special cams. Moreover, high pressure steam and compressed air were not available.

The method of regulation finally adopted is based on an apparatus recently developed by Warren (1) for producing a controlled temperature program in a muffle furnace. He employs conducting strips of aluminium foil cemented on to the chart of a potentiometric recorder, the strips being cut to conform to a definite temperature-time gradient, a stylus travelling between the strips which are separated by a distance of 0.16 mm. Resistances are so arranged that a falling temperature, resulting in the pen contacting with the lower strip, cuts out resistance, and a rising temperature adds resistance.

In applying this principle to humidity control, a sufficient current is supplied to the direct resistance boiler to maintain it slightly below the boiling point. As the humidity in the cabinet falls, the wet bulb pen contacts with a conducting strip on the chart, operating a relay which shorts out the resistance in the boiler circuit. Steam is thus generated instantaneously, stopping the moment the pen leaves the conducting surface. It is thus possible to make the wet bulb record follow any predetermined course, rising, falling or constant. In the case of a falling curve it is, of course, necessary to continuously remove water at a suitably regulated rate. This can be readily controlled by the valve and timing arrangement previously described.

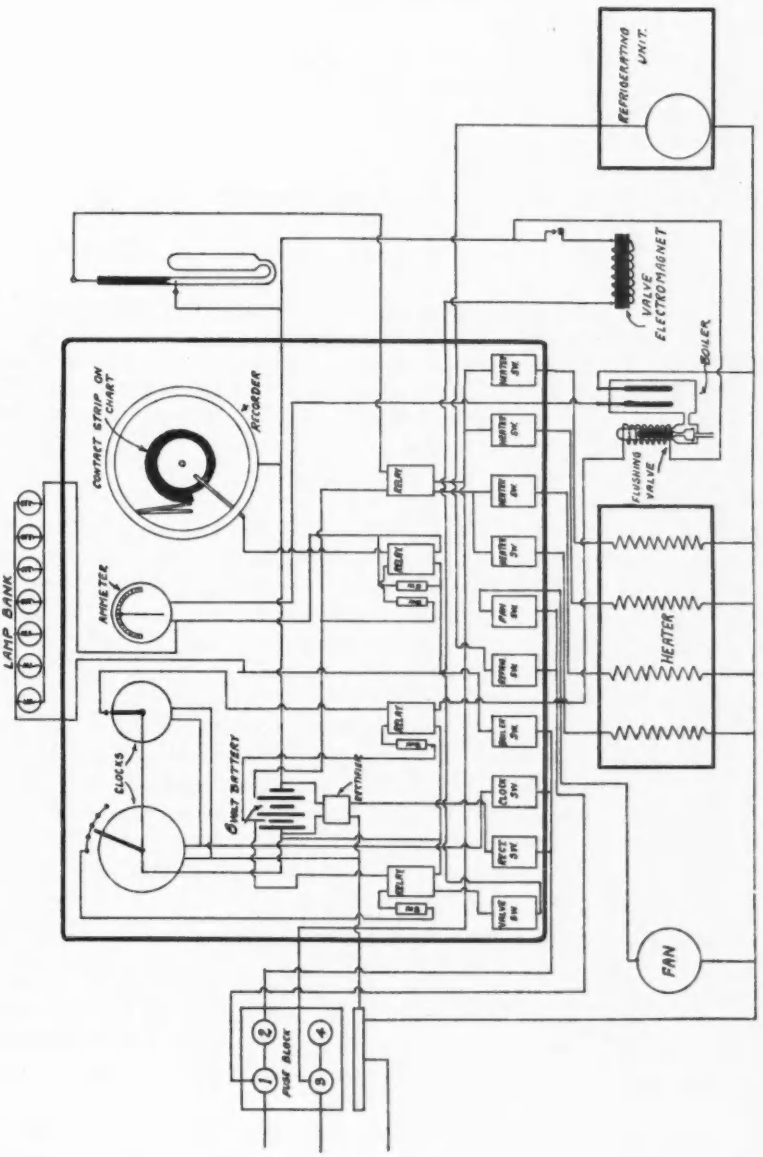

FIG. 5. *Wiring diagram.*

The principle of adding and withdrawing moisture simultaneously to maintain a desired relative humidity is analogous to that employed in maintaining a thermostat below room temperature by the combined use of heating and cooling devices.

Considerable difficulty was experienced in securing a satisfactory contact surface; aluminium foil as used by Warren (1) could not be cut and fitted with sufficient accuracy to a circular chart, gave poor electrical contact, and also obstructed the free travel of the pen. Satisfactory results were finally attained by two methods, the first being suited to the production of a chart required once only, the second for a permanent chart that may be used repeatedly.

Method I

Precipitated copper powder is mixed with a cellulose lacquer, painted on to the chart in a strip, the outer edge of which conforms to the required curve, dried, and burnished until a conducting surface is obtained. Some little experience is necessary to secure uniform results by this method and the charts deteriorate rather rapidly, generally losing their conducting power after a few days.

Method II

The required curve is plotted on a paper chart and a circular disk of celluloid superimposed. This disk is provided with a central hole of the same size as the chart, the two being clamped together on a metal plate by means of a central bolt or mandril. The conducting strip is then painted on to the celluloid as in Method I. When dry it is burnished, a conducting wire attached, and copper-plated in a cyanide bath, using a large circular sheet of the metal as an anode. With a $\frac{1}{2}$ in. separation approximately 30 min. with a current of 0.15 amp. is satisfactory. Too heavy a plate tends to cause the coating to peel. The copper powder is prepared by gradually adding zinc dust to copper sulphate solution, stirring vigorously until nearly decolorized, washing with dilute hydrochloric acid, followed by water until free from acid. The precipitated metal is then transferred to a Buchner funnel, washed with alcohol and ether and stored under c.p. amyl acetate until required.

A suitable cellulose lacquer may be prepared by dissolving celluloid clippings in a mixture comprised of equal volumes of amyl acetate, ethyl acetate and acetone and adding 1 to 2% of dibutyl phthalate as a plasticizer. The mixture of copper powder and lacquer is made in a small agate mortar and only as required, a reaction apparently taking place which causes a gradual thickening, thus impairing its working qualities and affecting the conductivity.

An adjustable brush contact is fitted to the case of the recorder, the wet bulb pen itself completing the circuit. Ink may be used in this pen without interfering with its function as a contact. A two volt current is employed

to actuate a standard "Pony" telegraph relay, fitted with heavy wiring and large silver contacts. This relay controls the resistance employed to regulate the idling current on the boiler, which consists of a bank of 100-watt lamps. A current of approximately 1.4 amperes is sufficient to maintain the temperature just below the boiling point.

This control functions very smoothly; no appreciable deviation of the wet bulb pen from the contact edge can be observed and any form of curve is accurately followed, the only limit to the steepness of falling gradient obtainable being imposed by the rapidity with which the refrigerator can remove moisture. This same method of control may be employed to produce a rising temperature-time gradient by placing the contact strip above the dry bulb pen, and connecting to the heater relay in place of the thermoregulator.

Operation

The operation of the whole assembly in drying a charge of macaroni or spaghetti is as follows. The required humidity-time curve is plotted and humidities read off and tabulated for each hourly interval. The desired dry bulb temperature is then selected and the hourly humidities calculated to the corresponding wet bulb temperatures. These temperatures are then plotted on a recorder chart (or charts) and a control chart prepared by either Method I or II. Air circulation is then started, the temperature raised to the desired value and the thermoregulator adjusted. When constancy of dry bulb temperature has been attained, steam is admitted until saturation is reached, the air flow checked with a small diaphragm and the charge introduced. The resistance on the boiler is then regulated to maintain approximate saturation and the charge allowed to come to equilibrium (about two hours). The control chart is then fitted, the refrigerator started, and the valve control set for appropriate time intervals; the diaphragm is removed and the boiler resistance readjusted. Drying now proceeds automatically according to the predetermined schedule. The only necessary attention needed is to change the control chart if the drying schedule exceeds 24 hr. and possibly to defrost the cooling coils towards the end of a long run.

Acknowledgments

The authors are indebted to the staff of the Engineering Department of the University of Manitoba for valuable suggestions and assistance in the construction of the apparatus. They are also indebted to Mr. Eric Able for the suggestion from which the valve control was finally developed.

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THE PRECIPITIN RING TEST APPLIED TO SOME USTILAGINACEAE[1]

By E. C. Beck[2]

Abstract

The standard precipitin ring test was applied in an effort to differentiate the following smut fungi: (1) monosporidial cultures of *Sorosporium reilianum* (Kühn) McAlp., *Ustilago hordei* (Pers.) K. & S., *Ustilago levis* (K. & S.) Magn., *Ustilago zeae* (Beck.) Ung., and (2) mass cultures of *Ustilago hypodites* (Schlecht.) Fr., *Ustilago tritici* (Pers.) Rost., *Ustilago avenae* (Pers.) Jens., *Ustilago levis* (K. & S.) Magn., and *Ustilago zeae* (Beck.) Ung. The results obtained indicate that monosporidial strains could be satisfactorily differentiated. Although they were frequently mutually reactive in undiluted serum-antigen mixtures, their specificity was apparent in the persistence of the precipitin ring at greater dilutions with homologous than with heterologous mixtures. Mass cultures were not so satisfactorily differentiated and showed many cross reactions. The results indicate that closely related species and physiological forms of fungi are not easily differentiated since characters common to two or more of them apparently tend to mask their ultimate differences. The method, however, offers possibilities as regards the more intimate affinities among groups of doubtful species or genera.

Introduction

The present investigations were undertaken in an attempt to determine the usefulness of the precipitin ring test in the identification of fungi. The general limits of its usefulness were to be determined by its applicability to the various species of Basidiomycetes, the Ustilaginales and Uredinales, and if the results thus warranted, the method was to be extended to the differentiation of physiological forms within the species previously employed.

While this study was in progress Link and Wilcox (6, 7) reported on extensive investigations along the same general line. Since these have shown very satisfactorily the limitations of the method in differentiating various species and strains of the Fungi Imperfecti, it has been decided to discontinue the project, and to publish the preliminary results which have been obtained to date and which are in general accord with those obtained by Link and Wilcox.

Materials and Methods

The cultures of monosporidial origin from which extracts were obtained were procured through the courtesy of Dr. J. J. Christensen of Minnesota University, and are designated by the superscript letter C, namely *Ustilago zeae*[C], *Ustilago hordei*[C], *Ustilago levis*[C] and *Sorosporium reilianum*[C]. The culture of *Ustilago hypodites* was isolated from *Agropyron repens*, collected and identified by Dr. R. E. Fitzpatrick of this department. *Ustilago zeae* was isolated from corn collected in a nearby field. The remainder, namely *Ustilago avenae*, *Ustilago tritici* and *Ustilago levis* were isolated from materials provided by Professor J. E. Howitt, of the Ontario Agricultural College, Guelph.

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Contribution from the Department of Botany, University of Toronto, Toronto, Ontario, Canada.

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In making the isolations from the mass cultures, monospory was not attempted, as it was thought that a comparison of bulk cultures with those of monosporidial origin might reveal some interesting differences. Spores were removed by means of sterile forceps from the inside of smut galls, and transferred to the following smut medium recommended and used by Stakman, Christensen *et al.* (9): potato extract, 1.8% agar, 1.0% dextrose, 1.0% sucrose and 1.0% malt extract. The medium was dispensed in eight-ounce medicine bottles and incubated at 26° C. for two days prior to inoculation.

After inoculation the cultures were incubated at 26° C. for two weeks, during which time a heavy mass of growth developed over the entire surface of the medium. This surface growth being in most cases cohesive, was easily removed by means of a stout lance-shaped needle. Those less cohesive were washed from the agar surface by means of 0.85% sodium chloride solution and removed to a sterile mortar and ground in fine, chemically clean sterilized quartz sand. To each inoculum was added 50 cc. of 0.85% sodium chloride solution. The resulting finely ground product was digested in the ice box for 18 hr. before being filtered under pressure through a layer of glass wool which was covered with filter paper in a Büchner filter. The filtrate was filtered through No. 4 Mandler bacteria-proof filters. The crystal clear extracts which resulted were dispensed in 5-cc. vaccine bottles and stored in the ice box when not in use.

In order to determine whether the medium exudate was an influencing factor in the tests, a sufficient quantity of the fluid exuded from the sterile agar was collected and used for immunization, and the resulting antiserum was tested in series with the fungus antisera.

It was found unnecessary, as suggested by Link and Wilcox (7), to remove the lipoids from the fungus material in order to procure clear extracts. However the finely ground fungus material, on account of its cohesiveness, presented difficulty in the filtering process and necessitated the use of two or more Mandler filters.

Before administering the first injection to the rabbit to be immunized, 1.0 cc. of blood was taken from the marginal vein of one ear, and 0.5 cc. of the immunizing fluid was injected into the marginal vein of the other ear. The serum was removed from the blood clot and tested with the extract. None of the serum collected in this way gave a precipitin reaction. After the initial injection of 0.5 cc., seven subsequent intravenous injections of 1.0 cc. were given at intervals of one day. When the initial dose was increased to 1.0 cc. the animal sustained a severe shock which delayed further immunization for at least one week. Ten days after the last injection the animals were starved for 24 hr., chloroformed and bled from the heart by means of a sterile 50-cc. syringe with a No. 20 long needle. A method involving less experimental risk, especially when only one animal is available for immunization against an extract, would have been to take 10 to 20 cc. of blood from the ear vein and to repeat the operation after a day or so. No preservatives were added to the serum after its removal from the blood clot, or to the antigens. This necessitated most scrupulous aseptic technique.

In conducting the tests, serum dilutions were prepared with 0.85% sodium chloride solution in 0.5-cc. amounts, each of which was carefully overlaid with 0.5 cc. of antigen. Though this method of preparing the tests does not give the maximum titre, it does permit of more extensive tests from the same amount of antiserum than when the order of dilution is reversed. The controls set up with each test were: No. 1, undiluted immune serum plus saline, and No. 2, saline plus antigen. Positive controls occurred only with the antiserum produced from *U. avenae* extract. Readings were made after one hour's incubation at 37° C.; the racks were then removed to the ice box and a second reading was made the following morning. In a few instances the later readings gave a positive test in a higher dilution, but one positive reaction in a dilution of 1:80 became negative overnight. After reading the ring test satisfactory shake tests were not obtained.

Results

The agar-extract antiserum was found to be specific for its homologous antigen giving no cross reactions. It can be concluded then that the medium was not an influencing factor of variation in the reactions.

Table I shows the reactions of the immune sera prepared from the four monosporidial cultures supplied by Dr. Christensen. In each test the immune

TABLE I

ANTISERUM-EXTRACT REACTIONS

Fungal extracts (antigens)	Serum dilutions							Serum dilutions						
	Serum + antigen	1:5	1:10	1:20	1:40	1:80	1:160	Serum + antigen	1:5	1:10	1:20	1:40	1:80	1:160
	Sorosporium reilianum[C]							*Ustilago hordei*[C]						
S. reilianum[C]	+	+	+	+	+	+	0	−	−	−	−	−	−	−
U. hordei[C]	+	+	+	0	0	0	0	+	+	+	+	+	+	+
U. levis[C]	+	+	+	0	0	0	0	0	0	0	0	0	0	0
U. zeae[C]	+	+	+	0	0	0	0	0	0	0	+	±	0	0
U. hypodites	+	+	0	0	0	0	0	−	−	−	−	−	−	−
U. tritici	+	+	0	0	0	0	0	−	−	−	−	−	−	−
U. avenae	+	+	0	0	0	0	0	−	−	−	−	−	−	−
U. levis	+	+	0	0	0	0	0	−	−	−	−	−	−	−
U. zeae	+	+	0	0	0	0	0	−	−	−	−	−	−	−
Medium exudate	−	−	−	−	−	−	−	0	0	0	0	0	0	0
	Ustilago levis[C]							*Ustilago zeae*[C]						
S. reilianum[C]	0	0	0	0	0	0	0	0	0	0	0	0	0	0
U. hordei[C]	+	+	+	+	±			0	±	0	0	0	0	0
U. levis[C]	+	+	+	+	+	+	±	0	0	0	0	0	0	0
U. zeae[C]	+	0	0	0	0	0	0	+	+	+	+	+	+	0
U. hypodites	0	0	0	0	0	0	0	0	0	0	0	0	0	0
U. tritici	±	±	0	0	0	0	0	+	+	+	+	+	±	0
U. avenae	±	±	0	0	0	0	0	+	+	+	+	+	±	0
U. levis	±	0	0	0	0	0	0	0	+	+	+	0	0	0
U. zeae	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Medium exudate	±	0	0	0	0	0	0	0	0	0	0	0	0	0

Note: + = *definite precipitin ring;* ± = *doubtful;* − = *no test;* 0 = *negative.*

serum plus its homologous antigen gave a ring test in a higher dilution than with any of the three heterologous antigens; the difference in each instance showing a specificity which would permit species differentiation. Thus *U. zeae*^{C} was completely specific. *U. levis*^{C} immune serum gave two cross reactions, *i.e.*, *U. hordei*^{C} (1:20) and *U. zeae*^{C} (serum plus antigen). The serum of *U. hordei*^{C} reacted with *U. zeae*^{C} antigen (1:20). Cross reactions occurred in *S. reilianum* serum, with the three heterologous antigens (1 : 10).

As for the reactions of the remaining five antisera (Table II), the results indicate less specificity. *U. levis* antiserum showed positive with its homo-

TABLE II

ANTISERUM-EXTRACT REACTIONS

Antigens	Serum dilutions							Serum dilutions						
	Serum + antigen	1:5	1:10	1:20	1:40	1:80	1:160	Serum + antigen	1:5	1:10	1:20	1:40	1:80	1:160
	Ustilago hypodites							*Ustilago tritici*						
S. reilianum^{C}	—	—	—	—	—	—	—	0	0	0	0	0	0	0
U. hordei^{C}	0	0	0	0	0	0	0	0	0	0	0	0	0	0
U. levis^{C}	—	—	—	—	—	—	—	0	0	0	0	0	0	0
U. zeae^{C}	—	—	—	—	—	—	—	+	+	+	0	0	0	0
U. hypodites	+	+	+	±	0	0	0	+	+	+	+	0	0	0
U. tritici	+	0	0	0	0	0	0	+	+	+	+	+	0	0
U. avenae	—	—	—	—	—	—	—	0	0	0	0	0	0	0
U. levis	—	—	—	—	—	—	—	0	0	0	0	0	0	0
U. zeae	—	—	—	—	—	—	—	+	+	+	0	0	0	0
Medium exudate	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Ustilago avenae							*Ustilago zeae*						
S. reilianum^{C}*	+	+	+	±	±	0	0	0	0	0	0	0	0	0
U. hordei^{C}	+	0	0	0	0	0	0	+	0	0	0	0	0	0§
U. levis^{C}	±	0	0	0	0	0	0	0	0	0	0	0	0	0
U. zeae^{C}	+	+	0	0	0	0	0	+	+	+	±	0	0	0§
U. hypodites†	+	+	+	+	+	±	0	+	+	+	+	0	0	0
U. tritici†	+	+	+	±	0	0	0	0	0	0	0	0	0	0
U. avenae	+	+	+	+	+	0	0	0	0	0	0	0	0	0
U. levis	+	+	+	+	0	0	0	+	+	+	0	0	0	0
U. zeae	+	+	0	0	0	0	0	+	+	+	+	0	0	0§
Medium exudate	0	0	0	0	0	0	0	—	—	—	—	—	—	—
	Ustilago levis							Agar exudate						
S. reilianum^{C}	0	0	0	0	0	0	0	—	—	—	—	—	—	—
U. hordei^{C}	0	0	0	0	0	0	0	0	0	0	0	0	0	0
U. levis^{C}	0	0	0	0	0	0	0	0	0	0	0	0	0	0
U. zeae^{C}	+	±	0	0	0	0	0	0	0	0	0	0	0	0
U. hypodites	+	+	0	0	0	0	0	—	—	—	—	—	—	—
U. tritici	+	+	+	0	0	0	0	—	—	—	—	—	—	—
U. avenae	0	0	0	0	0	0	0	—	—	—	—	—	—	—
U. levis	+	+	+	+	+	+	+	0	0	0	0	0	0	0
U. zeae	0	0	0	0	0	0	0	—	—	—	—	—	—	—
Medium exudate	—	—	—	—	—	—	—	+	+	+	+	+	+	+

*= ± *No. 1 control;* †= + *No. 1 control;* §= *negative on second reading.*

logous antigen when diluted 1 : 160 and gave cross reactions with the antigens of *U. tritici* and *U. hypodites* in dilutions of 1 : 10 and 1 : 5 respectively. *U. tritici* antiserum showed positive in a dilution of 1 : 80 with its own antigen and reacted also with *U. hypodites* (1 : 20), *U. zeae*^{C} (1 : 10), and *U. zeae* (1 : 10). The reactions in this instance as in the case of *U. levis* antiserum may be considered definite enough in differentiating the species. The immune serum of *U. avenae* gave a homologous reaction of 1 : 40 and a cross reaction with *U. levis* (1 : 20). The only doubtful controls were encountered in this test. It was felt that the results of the *U. hypodites* tests were inadequate because of having insufficient antiserum to complete the tests. The necessity of immunizing animals in duplicate is well brought out at this point. The low titre of *U. zeae* antiserum (1 : 20) may be explained by the failure of the animal to respond to immunization (4), or to the use of a less potent extract in producing the antiserum, but all of these tests need to be duplicated before deductions can be drawn. However, this seems undesirable inasmuch as the writer's results are in general agreement with those of Link and Wilcox, from which it seems evident that the precipitin ring test is not sufficiently specific for the purpose in mind, namely, the differentiation of closely related species and physiological forms. There is a suggestion in one result that this method might prove valuable in indicating the closer affinities among groups of doubtful species or genera.

Acknowledgments

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A DETERMINATION OF THE DISTORTION IN A NUMBER OF AIR CAMERA LENSES[1]

By R. H. Field[2]

Abstract

For map plotting purposes it is essential to know the principal distance (focal length) of air cameras, preferably for rays making various angles with the lens axis. A compact apparatus has been developed for making the necessary measurements and has been used for investigating the lens distortion in a number of air cameras. This method of finding distortion has the advantage that it takes into account the effect of the glass plate fitted in film cameras to maintain the film flat during exposure.

The distortion is given as the linear displacement in the plane of the photograph. It is felt that in this form the results are of more interest to those using air photographs. By simple calculations the figures can be changed to give the distortion in the forms more usual in the treatment of lens design.

Air photography makes severe demands on photographic lenses. The speed at which aircraft move relatively to the ground, the need for a maximum angular field of view in the interest of economy and the necessity for employing filters have resulted in air cameras being fitted with lenses having F/D ratios of four or less.

In applying the process of mapping from air photographs the most important fault in these lenses is distortion (2, pp. 48 and 63). Distortion results in a departure from the ideal perspective condition that point images in the picture plane subtend the same angle at the perspective centre as the corresponding points on the ground.

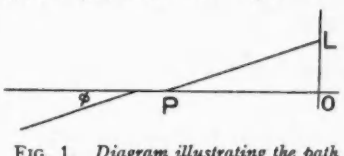

FIG. 1. *Diagram illustrating the path of a light ray in an air camera.*

P, Fig. 1, is the rear node of a lens and OL the plane of the negative, O being the foot of the perpendicular from P (*i.e.*, the "principal point" of the camera or photograph). A bundle of rays from a distant point makes an angle ϕ with OP and gives rise to an image L on the negative. In the ideal case angle OPL is equal to ϕ. Practically, if the distance OP be computed from the relation

$$OP = OL \cot \phi, \tag{1}$$

OL and ϕ being measured, the value of OP is found to vary with ϕ. As the position of the picture plane is fixed, it can be assumed that the position of the rear node, P, is not constant. For optical calculations the focal length of a lens is usually taken as the value of OP computed from Equation (1) when OL is infinitely small, while for map plotting purposes it is general to determine an average value of OP for the whole or a considerable portion of the angular field covered by the photograph. In this case the residuals between the value chosen and the actual value of OP at specific points are usually smaller (2, p. 64).

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Contribution from the Physical Testing Laboratories, Division of Physics, National Research Laboratories, Ottawa, Canada.
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The practical effect of the variation in the value of the principal distance, OP, is to give rise to changes in the scale of the photograph which depend on the zone in which images fall. If some particular value, OP, is taken for the principal distance, and is assumed to apply to the whole photograph, images where the true principal distance is $OP + \delta$ will be displaced radially on the photograph by an amount $\delta \tan \phi$, to a first approximation, from their nominal positions.

Each year, after overhaul, the principal distances of the cameras used by the Royal Canadian Air Force are determined in this laboratory. For such checks the observations need be made for one or two zones only, but on one occasion for most of the cameras they have been extended to cover the whole range of the picture. From these measurements some interesting data have been acquired regarding the distortion in lenses of differing design and focal length.

In the method which has been developed in this laboratory for determining the principal distance, a rectangular glass plate engraved with two diametral lines, crossed by short lines accurately placed at centimetre intervals, is held against the glass focal plane plate of the camera with the aid of simple devices, which vary slightly with different forms of camera. The angle ϕ (Fig. 1) is then measured with the aid of a theodolite reading to single seconds, measurements being made (in the special determinations) at each centimetre from O to the edge of the camera opening.

Fig. 2 is a sketch of the apparatus. The camera is mounted with the axis of the lens horizontal on a stand supported by three footscrews; two of these rest in grooved rails and the third is supported on a plane rail. Two round rails, approximately perpendicular to those supporting the camera-stand,

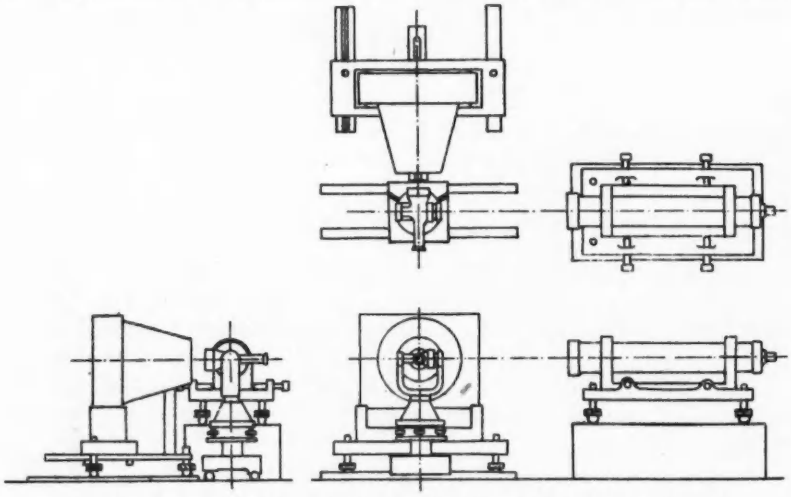

FIG. 2. *Plan and elevations of apparatus for determining the lens constants of air cameras.*

bear a cast iron sliding member which supports the theodolite. Both the camera and theodolite stands are sufficiently massive that, with ordinary care on the part of the observer, observations are concordant and there is no necessity for clamping. Thus the theodolite can be placed quickly in the correct position to sight through the camera lens on to one of the graduation marks of the glass plate.

A collimator, serving as a reference azimuth for the angles measured, is arranged almost collinear with the direction of the rails supporting the theodolite, at about the same height as the axes of the theodolite telescope and camera, when all three axes are horizontal. The various adjustments required can be made rapidly to the necessary degree of accuracy. Concrete piers support the whole apparatus in a room subject to very small temperature fluctuations.

To simplify calculations the glass plate is first located with the camera focal plane plate accurately leveled over a mercury surface. Using an autocollimating eyepiece the plate is adjusted until the intersection of the diametral lines, seen through the eyepiece, coincides with the image reflected from the mercury. The intersection should then be at the principal point. It is stated (1, p. 54) that this method is liable to error arising from centering errors in the lens components. An error of this nature should show itself by differences in the angles subtended by the nearer marks equally spaced on either side of the intersecting diametral lines (1, p. 26). In the lenses so far examined no appreciable effect of this nature has been found.

After the plate has been located and clamped, the camera is placed on its support and the lens axis and horizontal line on the plate are brought to true horizontality with the aid of the footscrews, the operation being controlled by observations through the theodolite telescope. Horizontal angles between the graduation marks and the collimator axis are then measured, one mark at a time. For each measurement the telescope is adjusted so as to point close to the centre of the lens opening. As the marks approach the edges this adjustment is best controlled by viewing the exit pupil of the telescope through a small magnifier and moving the theodolite until the meniscus formed by the lens aperture appears centrally placed.

Check observations are made on the intersection of the diametral lines at the end of each set, and, more nearly to equalize the weights, additional pointings are made on the graduations nearer the intersection, where the measured angles are small and the computed distances subject to greater error.

In each set of observations angles are measured on both diameters of the graduated plate, *i.e.*, in four directions outward from the principal point, and the mean value of the principal distance is computed for each zone from Equation (1). For one or two lenses a small systematic difference was found between some of the measurements along different radii, and it was concluded that the distortion was not quite symmetrical.

The results of the observations so far concluded are shown in Table I. In each case the mean value of the principal distance was the mean of the values

computed for the eight groups of points, 1 to 8 cm. distant from the principal point. Distortion was computed from the difference between this mean and the actual computed principal distance for the radius in question. A plus sign signifies distortion away from the centre.

TABLE I

DISTORTION IN MICRONS IN THE PLANE OF THE NEGATIVE

No.	Principal distance, mm.	Distance from principal point, mm.										F/D
		10	20	30	40	50	60	70	80	90	100	110	
"Xpress" lenses													
119798	208.93	+ 5	+ 8	+10	+ 4	− 7	−14	−30	−42	−52	−58	−84	4.5
123427	209.56	+ 1	+ 5	+ 9	− 2	− 2	−14	− 7	−23	−52	−53	−58	4.5
123428	209.74	+ 3	+ 8	+ 7	+ 4	− 7	−14	−17	−23	−26	−62	−58	4.5
123429	209.73	+ 3	+ 4	+ 4	− 2	− 2	−12	−10	−23	−48	−62	−63	4.5
123430	209.63	+ 6	+ 8	+10	+ 2	−14	−26	−27	−31	−65	−67	−79	4.5
126715	211.06	+ 4	+ 4	+ 6	− 4	− 9	− 8	−10	−19	−42	−42	−41	4.5
126718	210.99	+ 5	+ 7	+ 7	0	− 5	−20	−20	−26	−47	−75	−145	4.5
126719	211.23	+ 4	+ 3	+ 8	+ 2	− 7	−14	−16	−23	−38	−66	−78	4.5
126727	211.54	+ 3	+ 5	+ 6	0	−12	−11	−13	−23	−34	−61	−67	4.5
123447	303.37	− 1	+ 1	+ 6	+ 3	0	0	− 7	−13	−24	−40	−54	4
126889	511.70	+ 1	+ 5	+ 5	+ 3	0	− 2	−14	−23	−37	−55	−64	4
"Dagor" lenses													
396769	210.01	− 4	− 4	− 1	0	+ 2	0	+13	+23	+43	+62	+79	6.8
398305	210.50	− 5	− 5	− 9	− 6	+ 2	+ 9	+20	+38	+60	+86	+115	6.8
399219	209.29	− 2	− 5	− 7	−10	− 2	+ 3	+20	+38	+52	+77	+111	6.8
399221	207.25	− 4	−10	− 4	− 4	+ 7	+ 9	+24	+38	+60	+72	+132	6.8
399223	209.41	− 2	− 7	− 9	− 4	+ 5	+12	+17	+39	+48	+86	+111	6.8
399224	208.40	+ 1	− 2	− 3	−13	−17	+12	+20	+31	+65	+38	+16	6.8
399241	206.33	− 3	− 3	− 4	+ 2	− 5	0	+13	+27	+52	+82	+106	6.8
399249	208.56	− 4	− 5	− 7	− 2	+ 7	+ 9	+13	+23	+43	+62	+84	6.8
399253	207.45	− 3	− 3	− 9	− 4	+ 7	+ 6	+10	+23	+17	+48	+84	6.8
751117	208.62	− 2	− 3	− 4	− 2	− 2	0	+ 7	+31	+65	+86	+127	6.8
751131	209.02	0	− 2	− 9	−19	− 5	+14	+13	+31	+48	+67	+100	6.8
752160	209.21	− 4	− 7	− 4	− 2	+ 5	+ 9	+17	+27	+30	+43	+79	6.8
"Tessar" lenses													
726727	249.66	− 1	+ 5	+ 6	+10	+ 2	+ 2	−11	−38	−76	−132	−172	4.5
736720	249.64	+ 2	+ 6	+ 8	+ 5	+ 2	− 5	− 8	−48	−101	−160	−246	4.5
736721	249.79	+ 1	+ 5	+ 6	+ 6	+ 6	− 5	−20	−42	−90	−124	−198	4.5
737748	250.26	0	+ 4	+ 6	+ 5	+ 2	− 2	−11	−35	−79	−136	−220	4.5
422415	298.52	+ 3	+ 7	+ 9	+ 9	+ 2	− 8	−26	−48	−69	−117	−181	4.5
479890	297.91	− 1	0	+ 6	+12	+ 3	0	−12	−24	−58	−92	−146	4.5
484152	296.94	+ 4	+ 7	+11	+ 3	+ 7	−12	−31	−60	−104	−160	−224	4.5
512148	298.94	+ 3	+ 6	+10	+ 4	+ 2	−10	−26	−54	−87	−137	−199	4.5
642351	298.71	+ 2	+ 4	+ 6	+ 7	0	− 6	−16	−32	−54	−87	−147	4.5
660756	298.48	+ 1	0	+ 3	0	+ 3	− 2	− 5	−19	−30	−60	−87	4.5
664269	298.28	+ 2	+ 2	+ 6	+ 1	− 2	− 4	−16	−29	−33	−50	−114	4.5
674010	299.50	+ 2	− 1	+ 3	0	+ 2	− 4	− 5	−13	−36	−33	−40	4.5
674012	299.38	− 1	+ 3	+ 4	0	+ 2	0	0	− 5	−12	−26	−33	4.5
674013	298.71	− 1	+ 1	+ 3	+ 4	+ 2	+ 2	− 5	−11	−18	−44	−63	4.5
674015	298.95	+ 3	+ 4	+ 3	− 3	0	− 4	− 5	−29	−30	−33	−62	4.5
814523	297.63	+ 1	+ 5	+ 1	− 1	+ 3	0	−10	−16	−55	−85	−131	4.5
814570	296.97	+ 1	+ 3	+ 4	+ 4	0	0	−12	−27	−46	−82	−120	4.5
814571	297.58	+ 3	+ 4	+ 6	+ 4	0	−10	−17	−30	−43	−71	−105	4.5
670183	500.58	0	− 1	− 3	− 2	+ 4	− 1	0	+ 5	+ 2	−4	+ 4	5

Acknowledgment

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THE SOUND FIELD OF MEMBRANES AND DIAPHRAGMS

II. THE POWER EMITTED BY CIRCULAR MEMBRANES[1]

By R. Ruedy[2]

Abstract

Accurate formulas are presented showing the power radiated by a stretched circular membrane vibrating with small amplitudes and an arbitrary number of nodal circles or diameters. When the nodes are circular, the sound emitted is expressed as a sum of the products of simple functions of ka, $J_0(2ka)$, $J_1(2ka)$ by the definite integral of $y^{2n}/(\kappa^2a^2/k^2a^2-1+y^2)^2$ taken between the limits zero and unity. For values of $ka=2\pi a/\lambda$ between zero and two, where the radius a is taken as 10 cm., the membrane vibrating in its fundamental mode emits between three and four times as much power as the piston having the same maximum velocity at its centre. The first and second overtones have about the same strength as the corresponding fundamental frequencies, so the power radiated increases less rapidly with frequency than when nodes are absent.

Introduction

The strength of the sound emitted by diaphragms and membranes was studied when telephone receivers were developed. In view of the fact, however, that modern large-sized reproducers of speech and music, and the lines used for transmitting them over long distances, are expected to convey to the hearer a much wider range of frequencies than is necessary in reproducing simple conversation from person to person, it is of practical interest to study the question more thoroughly than before (1–4).

When the elements of a circular surface which is set into an infinite wall or baffle perform harmonic vibrations normal to the surface according to a function $w(r, \phi)$, the total power emitted from one side can be computed by two different methods. The usual solution is to put the rate at which the source does work equal to the sum of the products of pressure variation by the particle velocity at the surface, using root mean square values for both, the pressure variation at any one point being itself the resultant of the pressure exerted upon the element by all the other points (Lord Rayleigh, I. B. Crandall). Except for perfectly plane waves the total pressure is found to possess a component in phase with the velocity, proportional to the power radiated, and a lagging component, proportional to the mass of the air set into motion (so-called accession to inertia).

On the other hand, when air damping is neglected, the power of the source in producing sound waves must be the same when integrated over any distant spherical surface of radius R, having the source of radius a at its centre, and equal to the mean sum of the products of alternating pressure $p=-s\partial\Phi/\partial t$ and radial velocity $v=\partial\Phi/\partial r=kp/s$ over the entire surface of one side of the disk, Φ being the velocity potential. Here s is the density in

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[2] *Research Investigator, National Research Laboratories, Ottawa.*

grams per cubic centimetre and $k=2\pi/\lambda$. With

$$\Phi = -\frac{e^{i(pt-kR_o)}}{2\pi R_o}\int_{\phi=0}^{2\pi} d\phi \int_{\gamma=0}^{\pi/2} ipw(r,\phi)\, e^{ikl} r\, dr \sin\gamma\, d\gamma,$$

γ being the angle which the chosen direction forms with the normal to the disk, the power emitted by the source becomes

$$E = \frac{c\rho}{2\lambda^2}\int_0^{2\pi} d\phi \int_0^{\pi/2} d\gamma \sin\gamma \left[\int_0^a \int_{\phi=0}^{2\pi} \dot{w}(r,\phi) r\, dr\, d\phi\, e^{ikl}\right]^2,$$

and the mass of the air to be displaced is $-c\rho/4\pi i\lambda R_o$ multiplied by the fourfold integral. The length l is equal to $r \sin\gamma \cos\phi$.

The Rigid Piston

If we take the rigid piston as a basis of comparison, all the surface elements possess the same amplitude, $\dot{W}_o$, of velocity and the same phase, and since

$$J_o(u) = \frac{2}{\pi}\int_0^{\pi/2} \cos(u\cos\phi)\, d\phi = \frac{1}{2\pi}\int_0^{2\pi} \cos(u\cos\phi) d\phi$$

and

$$\int_0^r r^{n+1} J_n(r) dr = r^{n+1} J_{n+1}(r),$$

it follows that as far as real quantities are concerned

$$\int_0^{r=a}\int_{\phi=0}^{2\pi} e^{ikl} r\, dr\, d\phi = \int_0^a \int_0^{2\pi} r\, dr \cos(kr\sin\gamma\cos\phi) d\phi = 2\pi \int_0^{r=a} r J_o(kr\sin\gamma) dr = 2\pi a^2 \frac{J_1(ka\sin\gamma)}{ka\sin\gamma}.$$

Hence

$$E = \frac{4\pi^2 a^4}{\lambda^2} c\rho \frac{\dot{W}_o^2}{2}\int_0^{2\pi} d\phi \int_0^{\pi/2} d\gamma \sin\gamma \frac{J_1^2(ka\sin\gamma)}{(ka\sin\gamma)^2}.$$

Taking into account the relation

$$J_n^2(y) = \sum_{m=o}^{\infty} (-1)^m \frac{\Gamma(2n+2m+1)}{\Gamma(m+1)\Gamma(2n+m+1)\Gamma^2(n+m+1)} \left(\frac{y}{2}\right)^{2n+2m},$$

$$J_1^2(ka\sin\gamma) = \sum_{m=o}^{\infty} (-1)^m \frac{\Gamma(2m+3)(ka)^{2m+2}}{\Gamma(m+1)\Gamma(m+3)\Gamma^2(m+2)} \frac{\sin^{2m+2}\gamma}{2^{2m+2}},$$

where the symbol Γ indicates the gamma function, which reduces in the present case to mere factorials, therefore

$$\int_0^{\pi/2} \frac{J_1^2(ka\sin\gamma)}{k^2a^2\sin^2\gamma} \sin\gamma d\gamma = \sum_{m=o}^{\infty} (-1)^m \frac{\Gamma(2m+3)(ka)^{2m}}{2^{2m+2}\Gamma(m+1)\Gamma(m+3)\Gamma^2(m+2)} \int_0^{\pi/2} \sin^{2m+1}\gamma d\gamma.$$

As $(2m+1)$ is an odd number the integral becomes equal to $2^m\Gamma(m+1)/1.3.5\ldots(2m+1)$, and finally

$$E = \pi a^2 c\rho k^2 a^2 \frac{\dot{W}_o^2}{2}\left(\frac{1}{1.2} - \frac{k^2a^2}{1.2^2.3} + \frac{k^4a^4}{1.2^2.3^2.4} - \frac{k^6a^6}{1.2^2.3^2.4^2.5}\cdots\right)$$

or

$$E = c\rho\pi a^2\left(1 - \frac{J_1(2ka)}{ka}\right)\frac{\dot{W}_o^2}{2},$$

a formula which is in agreement with the result obtained by the first method.

Power Emitted by the Circular Membrane

In the case of the circular membrane, or drumhead, firmly clamped at the edge, the directional properties of the pressure amplitude are determined by the derivative of the velocity potential Φ with respect to time (4). For even values of n

$$\Phi = -2\pi a^2 \kappa_{nm} a J_{n-1}(\kappa_{nm}a)\frac{A'_{nm}}{2\pi R_o}\cos n\phi \frac{J_n(ka\sin\gamma)}{\kappa_{nm}^2 a^2 - k^2a^2\sin^2\gamma},$$

leaving out the factor $e^{i(pt-kR_o)}$; and the main difference with regard to the piston is the fraction containing J_n which must be squared and integrated over the entire hemisphere of radius R_o. This gives

$$E = 4\pi^2 a^4 \kappa_{nm}^2 a^2 \frac{c\rho}{2\lambda^2} J_{n-1}^2(\kappa_{nm}a) A'^2_{nm} \int_{\phi=0}^{2\pi} d\phi \cos^2 n\phi \int_{\gamma=0}^{\pi/2} d\gamma \sin\gamma \frac{J_n^2(ka\sin\gamma)}{(\kappa_{nm}^2 a^2 - k^2a^2\sin^2\gamma)^2}.$$

With $x = \sin\gamma$ and $dx = \sqrt{1-x^2}\,d\gamma$, and taking into account the relation

$$\int_0^{2\pi}\cos^2 n\phi\, d\phi = \int_0^{2\pi}\sin^2 n\phi\, d\phi = \pi,$$

except when $n=0$, in which case the first integral is equal to 2π,

$$E = \frac{\kappa_{nm}^2 a^2}{k^2a^2} c\rho\pi a^2 J_{n-1}^2(\kappa_{nm}a)\frac{A'^2_{nm}}{2}\int_0^1 \frac{xJ_n^2(kax)dx}{\left(\frac{\kappa^2a^2}{k^2a^2} - x^2\right)\sqrt{1-x^2}}.$$

Now

$$\int \frac{xJ_n^2(kax)dx}{\left(\frac{\kappa^2a^2}{k^2a^2} - x^2\right)^2\sqrt{1-x^2}}$$

$$= \sum_{m=0}^{\infty}(-1)^m \frac{\Gamma(2n+2m+1)}{\Gamma(m+1)\Gamma(2n+m+1)\Gamma^2(n+m+1)}\left(\frac{ka}{2}\right)^{2(n+m)}\int \frac{x^{2n+2m}xdx}{\left(\frac{\kappa^2a^2}{k^2a^2} - x^2\right)\sqrt{1-x^2}}.$$

With $y^2 = 1-x^2$ the last integral becomes

$$\int_0^1 \frac{(1-y^2)^{n+m}}{\left(\left(\frac{\kappa^2a^2}{k^2a^2}-1\right)+y^2\right)^2}\,dy$$

$$= \int_0^1 \frac{1-\frac{(n+m)}{1!}y^2+\frac{(n+m)(n+m-1)}{2!}y^4-\frac{(n+m)(n+m-1)(n+m-2)}{3!}y^6\cdots}{(q^2+y^2)^2}\,dy.$$

Depending upon whether $\frac{\kappa^2a^2}{k^2a^2} \lesseqgtr 1$, when s is an even number.

$$\int \frac{y^s}{(q^2+y^2)^2} = \frac{(s-1)}{q^2+y^2}\left(\frac{y^{s-1}}{(1-s)(3-s)}-\frac{q^2y^{s-3}}{(3-s)(5-s)}+\frac{q^4y^{s-5}}{(5-s)(7-s)}-\frac{q^6y^{s-7}}{(7-s)(9-s)}\right.$$

$$\left.\cdots\pm\frac{q^{s-2}y}{2}\right)\pm\frac{(s-1)q^s}{2q^2\sqrt{\pm q^2}}\begin{matrix}\tan^{-1}\\ \tanh^{-1}\end{matrix}\frac{y}{\sqrt{\pm q^2}}$$

where, for values of s greater than two, and $s/2$ an odd number, it is correct to use the plus sign before the last term and the opposite sign for the last term but one, while the reverse is true when $s/2$ is even. In the last term the positive sign applies to $\tan^{-1}$ and $\kappa^2a^2/k^2a^2 \lesseqgtr 1$; the negative sign goes with $\tanh^{-1}$ and $\kappa^2a^2/k^2a^2 \lesseqgtr 1$. If desired $\tanh^{-1}(1/q)$ may be replaced by $1/2 \log (x-q)/(x+q)$. Finally, when $\kappa^2a^2/k^2a^2 = 1$, only the first term of the equation is required. Introducing the limits,

$$\int_0^1 \frac{y^s}{(q^2+y^2)^2}\,dy = \frac{1}{2q^2}\left(1+\frac{q^2+1}{q}\tan^{-1}\frac{1}{q}\right)\frac{k^2a^2}{\kappa^2a^2},$$

$$-\int_0^1 \frac{y^s}{(q^2+y^2)^2}\,dy = \left(\frac{1}{2}-\frac{q^2+1}{q}\tan^{-1}\frac{1}{q}\right)\frac{k^2a^2}{\kappa^2a^2},$$

$$\int_0^1 \frac{y^s}{(q^2+y^2)^2}\,dy = (s-1)\,\frac{k^2a^2}{\kappa^2a^2}\left\{\frac{1}{(1-s)\,(3-s)}-\frac{q^2}{(3-s)\,(5-s)}+\frac{q^4}{(5-s)\,(7-s)}+\cdots\pm\frac{q^{s-2}}{2q^2}\right.$$

$$\left.\pm\frac{q^s\,(q^2+1)}{\pm\,2q^2\sqrt{\pm q^2}}\begin{matrix}\tan^{-1}\\ \tanh^{-1}\end{matrix}\frac{1}{\sqrt{\pm\,q^2}}\right\}$$

Where only circular nodes exist ($n=0$), the number s equals m, and

$$E_0 = \pi a^2 c\rho\, J_1^2(\kappa_{0m}a)\,\dot{A}_{nm}^2 \sum_{m=0}^{\infty}(-1)^m\,\frac{\Gamma(2m+1)}{\Gamma^2(m+1)}\,\frac{ka^{2m}}{2^{2m}}\,\frac{\kappa_{0m}^2a^2}{k_{0m}^2a^2}\int_0^1 \frac{1-\frac{my}{1!}+\frac{m(m-1)y^4}{2!}\cdots\pm y^m}{(q^2+y^2)^2}\,dy,$$

and where $n=2$ (two nodal diameters), $s=m+2$, so that

$$E_2 = \pi a^2 c\rho\, J_1^2(\kappa_{2m}a)\,\frac{\dot{A}_{2m}^2}{2}\sum_{m=0}^{\infty}(-1)^m\,\frac{\Gamma(2m+5)(ka/2)^{2m+4}}{\Gamma(m+1)\Gamma(m+5)\Gamma^2(m+3)}\,\frac{\kappa_{2m}^2a^2}{k_{2m}^2a^2}$$

$$\times\int_0^1 \frac{1-\frac{(m+2)y^2}{1!}+\frac{m(m+2)(m+1)y^4}{2!}+\cdots\pm y^{m+2}}{(q^2+y^2)^2}\,dy$$

and so on for a higher number of diametral nodes. The power contained in overtones in any mode of vibration is obtained by inserting the proper value of κ_{nm}, the integral remaining the same for any overtone for a given number of diametral nodes.

Discussion of Results

Since the resonance frequencies f_{nm} of the membrane are given by $f_{nm}=\frac{\kappa_{nm}a}{2\pi a}\sqrt{\frac{T}{s'}}$, where Tdl is the tension in dynes across a straight line of length dl drawn anywhere upon the membrane, s' the mass in grams per sq. cm. and $(\kappa_{nm}a)$ the solution of the equation $J_n(\kappa a)=0$ (see Table I), whatever the frequency, the following relation holds

$$cka/\kappa a = \sqrt{T/s'}$$

or

$$ka/\kappa a = af_{oo}/12754,$$

in other words equals a constant value for a given tension of the membrane.

In particular, ka equals unity for $\sqrt{T/s'}=c/\kappa a$, and $ka=\kappa a$ for $\sqrt{T/s'}=3.33\times 10^4$. As f_{oo} is equal to $0.383\sqrt{T/s'}\,/\,a$, it follows that a membrane of 10 cm. radius, for which $k_{oo}a$ is made equal to unity (or $ka/\kappa a=0.416$ and $q^2=4.784$), possesses a resonance frequency f_{oo} of 530 cycles per second corresponding to a wave-length in air of about 63 cm., and a membrane of the same dimensions, but stretched so as to give a value $k_{oo}a$ of 2.405, that is, equal to $\kappa_{oo}a$, and q^2 equal to zero, has a resonance frequency of about 1280 cycles per second ($\lambda=26$ cm.). But these values involve the highest tensions safely applicable to membranes of known materials, and in general, therefore, the value of $\kappa_{oo}a/k_{oo}a$ is larger than unity, q^2 remaining positive as the resonance frequency f_{oo} is varied by changing the tension applied to the membrane. A case in point is the modern type of electrostatic membrane speaker in which an aluminium alloy of exceptional strength is used. With a radius of 19 cm., a thickness of 0.0016 cm. and a total weight of five grams, the fundamental frequency observed is 130 cycles per second.

TABLE I

SOLUTIONS $\kappa_{nm}a$ OF THE MEMBRANE EQUATION $J_n(\kappa a)=0$

—	$m=0$	$m=1$	$m=2$	$m=3$	m
$n=0$	2.405	5.520	8.654	11.792	$(m+\frac{1}{4})\pi$
$n=1$	3.832	7.016	10.137	13.233	$(m+\frac{1}{2})\pi$
$n=2$	5.135	8.417	11.620	14.796	$(m+\frac{3}{4})\pi$

Note :— m, number of circular nodes; n, number of nodal diameters.

(a) *Membrane Vibrating with its Fundamental Frequency*

In the case of the membranes for which, as indicated above, the value of $k_{oo}a$ is smaller than unity, the expression (κ^2a^2/k^2a^2-1) will be positive for all values of κ_{oo}, and the power radiated in ergs at various frequencies is, apart from the factor $\pi a^2 c\rho J_1^2(\kappa a)\dot{A}^2_{oo}$, given by

$$\Sigma=\left[1-\frac{2!}{1!^4}\left(\frac{\pi a}{\lambda}\right)^2+\frac{4!}{2!^4}\left(\frac{\pi a}{\lambda}\right)^4-1.\frac{6!}{3!^4}\left(\frac{\pi a}{\lambda}\right)^6+1.\frac{8!}{4!^4}\left(\frac{\pi a}{\lambda}\right)^8\right]\left[\frac{1}{2q^2}+\frac{q^2+1}{2q^2}\tan^{-1}\frac{1}{q}\right]$$

$$+\left[-\frac{2!}{1!^4}\left(\frac{\pi a}{\lambda}\right)^2+2.\frac{4!}{2!^4}\left(\frac{\pi a}{\lambda}\right)^4-3.\frac{6!}{3!^4}\left(\frac{\pi a}{\lambda}\right)^6+4.\frac{8!}{4!^4}\left(\frac{\pi a}{\lambda}\right)^8\cdots\right]\left[\frac{1}{2}-\frac{q^2+1}{2q}\tan^{-1}\frac{1}{q}\right]$$

$$+\left[\frac{4!}{2!^4}\left(\frac{\pi a}{\lambda}\right)^4-3.\frac{6!}{3!^4}\left(\frac{\pi a}{\lambda}\right)^6+6.\frac{8!}{4!^4}\left(\frac{\pi a}{\lambda}\right)^8\cdots\right]\left[1+\frac{3}{2}q^2-\frac{3}{2}\frac{q^2+1}{q}\tan^{-1}\frac{1}{q}\right]$$

$$+\left[-1.\frac{6!}{3!^4}\left(\frac{\pi a}{\lambda}\right)^6+8.\frac{8!}{4!^4}\left(\frac{\pi a}{\lambda}\right)^8\cdots\right]\left[-\frac{1}{3}+\frac{5}{3}q^2+\frac{5}{2}q^4-\frac{5}{3}q^3(q^2+1)\tan^{-1}\frac{1}{q}\right]$$

$$+\left[1.\frac{8!}{4!^4}\left(\frac{\pi a}{\lambda}\right)^8\cdots\right]\left[\frac{1}{5}-\frac{7}{5.3}q^2+\frac{7}{3.1}q^4+\frac{7}{2}q^6-\frac{7}{2}q^3(q^2+1)\tan^{-1}\frac{1}{q}\right]$$

for all values of $\pi a/\lambda$ smaller than 1.202 and modes of vibration involving circular nodes only. In evaluating the second bracket in each line advantage may be taken of the recurrence formula

$$\int\frac{y^s}{(q^2+y^2)^2}=-\frac{1}{(3-s)(q^2+1)}+\frac{s-1}{3-s}q^2\int\frac{y^{s-2}}{(q^2+y^2)^2}\,dy.$$

The infinite series occurring in the first bracket may be replaced if desired by the following simple functions of πa, $J_0(ka)$ and $J_1(ka)$:

$$1-\frac{2!}{1!^4}\left(\frac{\pi a}{\lambda}\right)^2+\frac{4!}{2!^4}\left(\frac{\pi a}{\lambda}\right)^4-\frac{6!}{3!^4}\left(\frac{\pi a}{\lambda}\right)^6+\frac{8!}{4!^4}\left(\frac{\pi a}{\lambda}\right)^8\cdots=J^2_o(ka)$$

$$\frac{2!}{1!^4}\left(\frac{\pi a}{\lambda}\right)^2+2\,\frac{4!}{2!^4}\left(\frac{\pi a}{\lambda}\right)^4-3\,\frac{6!}{3!^4}\left(\frac{\pi a}{\lambda}\right)^6+4\,\frac{8!}{4!^4}\left(\frac{\pi a}{\lambda}\right)^8\cdots=\frac{\pi a}{\lambda}\frac{dJ_o^2(ka)}{d(ka)}$$
$$=-kaJ_o(ka)J_1(ka)$$

$$\frac{4!}{2!^4}\left(\frac{\pi a}{\lambda}\right)^4-3\,\frac{6!}{3!^4}\left(\frac{\pi a}{\lambda}\right)^6+6\,\frac{8!}{4!^4}\left(\frac{\pi a}{\lambda}\right)^8\cdots=\frac{1}{2}\left(\frac{\pi a}{\lambda}\right)^2\frac{d}{d(ka)}\frac{\lambda}{\pi a}\frac{dJ_o^2(y)}{dka}$$
$$=\frac{ka}{4}\left\{ka(J_1^2(ka)-J_o^2(ka))+2kaJ_1J_o\right\}$$

$$-\frac{6!}{3!^4}\left(\frac{\pi a}{\lambda}\right)^6+8\,\frac{8!}{4!^4}\left(\frac{\pi a}{\lambda}\right)^8\cdots=\frac{ka}{1.2}(J_1J_o(2k^2a^2-4)-3kaJ_1^2+2kaJ_o^2)$$

and the next two series are

$$\frac{1}{4}\left(\frac{\pi a}{\lambda}\right)^7\frac{d}{d(ka)}\left(\frac{1}{3\pi a/\lambda}\frac{d}{d(ka)}\frac{1}{2\pi a/\lambda}\frac{d}{dka}\frac{1}{\pi a/\lambda}\frac{dJ_o^2(ka)}{d(ka)}\right)$$
$$=\frac{ka}{48}\left[(12-9k^2a^2)J_1J_o+(k^2a^2-6ka)J_o^2+(11ka-k^3a^3)J_1^2\right]$$

and

$$\frac{10!}{5!^4}\left(\frac{\pi a}{\lambda}\right)^{10}+\cdots=\frac{ka}{480}\left[(-96+88k^2a^2-4k^4a^4)J_1J_o+(48ka-13k^3a^3)J_o^2+(-100ka+15k^2a^2)J_1^2\right]$$

However, owing to the limited accuracy of the values of the Bessel functions found in the tables, when the variable ka is arbitrary there is little advantage in using the finite expressions in place of the series development except in the case of the first three or four expressions and small values of ka.

For very long waves, the power emitted on one side of the membrane becomes

$$E_\infty = \pi a^2 c\rho \frac{J_1^2(\kappa a)}{\kappa^2 a^2} \dot{A}_\infty^2 = 1.864\, \pi a^2 c\rho \dot{A}_\infty^2 \text{ ergs per sec.}$$

or over three times as much as would be obtained with a rigid piston having the same maximum velocity as the membrane possesses at its centre ($\dot{A} = \dot{W}$). When the tension applied to the membrane is increased and with it the resonance frequency, the power radiated assumes increasingly large values, as shown by Table II, which also shows for comparison the power radiated by the rigid piston of 10 cm. radius. (To find the power in absolute units (ergs), it is necessary to multiply the values given by $314.159\, c\rho\dot{A}^2$, where $c = 3.4 \times 10^4$ cm., $\rho = 0.0012$ gm. per cc. at 18° C. and 760 mm. Hg, and $\dot{A}$ is the maximum velocity or $6.28f$ times the maximum amplitude, usually a few mm.) For all values of ka larger than 0.1 and smaller than 2, the piston emits three or four times less power than the membrane.

TABLE II

POWER RADIATED BY A MEMBRANE OF 10 CM. RADIUS AT VARIOUS RESONANCE FREQUENCIES.

—	$ka=0.05$	$ka=0.10$	$ka=0.20$	$ka=0.40$	$ka=0.66$	$ka=1$	$ka=2$
$m=0$	0.0025	0.0081	0.034	0.153	0.411	0.896	2.51
$m=1$	—	—	—	—	0.075	0.17	—
$m=2$	—	—	—	—	0.03	0.07	—
Piston	—	0.0025	0.01	0.039	0.105	0.21	0.562

NOTE: m = *number of circular nodes.*

(*b*) *Membranes Vibrating with Several Circular Nodes*

The formula for the sound emitted by the membrane vibrating with its fundamental frequency also applies to the membrane vibrating with one or two circular nodes, except that the values of ka must be increased, in accordance with the higher frequency of the overtones, by the factor 2.29 for the first, and by the factor 3.6 for the second overtone. The result thus obtained shows that the power with which the harmonics are emitted between $ka=0$ and $ka=2$ is practically the same as has been found for the corresponding fundamental, so it increases less rapidly with frequency than it does in the fundamental mode of vibration. This decrease is to be expected in view of the opposition in phase shown by points situated at either side of the circular node.

A more complete discussion will be presented later together with the results obtained with diaphragms (thin plates).

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REVIEWS AND NOTES

A Thermostat for Temperatures between 5° and 20° C.

Constant temperatures lower than room temperature are frequently required, but few convenient means of producing them are available. The apparatus described here (Fig. 1) represents an adaptation of a thermostat described previously (1), and has been successfully employed in this laboratory for maintaining small objects at any constant temperature in this range. The essential part is a small Dewar flask (12 cm. in length) with a relatively wide clearance between the walls. This space is filled with mercury, which acts as the thermostat liquid and at the same time constitutes the thermoregulator, maintaining the space *A* at a constant temperature. A heating coil of 5 to 10 ohms resistance is wound directly on the glass (Pyrex). No relays or special circuits are required as the contact point simply short circuits the heating coil through the 50 watt lamp. No perceptible spark appears at the contact. The space *B* is filled with asbestos and is considerably larger in proportion to the Dewar than is shown in the diagram.

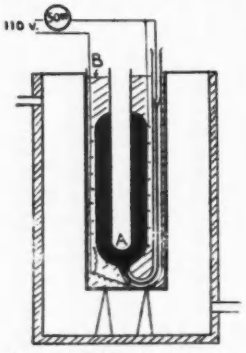

FIG. 1. *Thermostat for temperatures between 5° and 20° C.*

The whole apparatus is immersed in an insulated metal jacket through which cold water (4° C.) is circulated or which may be filled with ice. When the apparatus is properly constructed the temperature variations in *A* are scarcely detectable with a Beckmann thermometer, hence they are unlikely to be greater than 0.005° C.

The device has been used to produce constant vapor pressures in a sorption apparatus by immersing in it a bulb containing the liquid in question. When unlimited supplies of cold water are available the device may be operated continuously at temperatures below that of the room for long periods of time without attention.

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Improved Method for the Construction of Quartz Spirals

Quartz spirals for use in the McBain-Bakr sorption balance are generally made by winding a quartz fibre of suitable thickness on a carbon rod, using a small flame to soften the fibre at the appropriate point. Tapp (1) has described a system of gears which winds the spiral automatically. In all

cases, however, extreme care is required in handling the flame. If a flame hot enough to soften the fibre after it touches the rod is employed, there is danger of fusing the fibre before it is on the rod. On the other hand, if the flame is just sufficiently hot to soften the fibre in the air it is impossible to bend the fibre after it is on the rod owing to the heat loss by conductivity. The latter procedure has been the only safe one to employ, and it is apparent that the fibre must be bent to the correct curvature *before* it touches the rod. This requires very nice adjustment of the flame and the procedure is at best unsatisfactory.

The difficulty has been overcome by fluting the rod in such a way that the fibre touches at certain points only and the heat loss is thereby greatly reduced. The rod is placed in a lathe and longitudinal grooves are cut by racking the tool from side to side. A cross section of the rod after this treatment presents an appearance similar to a 10 or 12 pointed star. The fibre rides on the edges so formed and a large, comparatively cool, flame may be employed so that the fibre is heated on the rod for several turns back. Thus the fibre may be actually tightened while on the rod and there is much wider latitude in regard to the position of the flame. Some difficulty was experienced at first in removing the tightly wound spirals but this was obviated by turning a very slight taper on the rod before making the longitudinal grooves. With this modification the spiral slips off readily after being freed with a soft brush.

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